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THERMODYNAMICS OF METAL—LIGAND BOND FORMATION

XIX *. REACTION OF ARYLMERCURY HALIDES WITH LEWIS BASES

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Summary

Arylmercury halides react with 4-methylpyridine in benzene solution to form 1 : 1 adducts of low stability, $K \approx 2$ l mol^{-1}, $\Delta H^0 \approx -25$ kJ mol^{-1}. Much more stable adducts are formed with 1,10-phenanthroline or *N,N,N',N'*-tetramethyl-1,2-diaminoethane, usually $100 < K < 1000$, but their enthalpies of formation are little bigger, implying two rather weak Hg—N bonds are formed. Tertiary phosphines cause symmetrization and the enthalpies of reaction agree with those calculated from data for the heats of formation and solution of the species involved.

Introduction

While mercury(II) halides form addition compounds with a wide variety of Lewis bases, including those with nitrogen, phosphorus, arsenic or sulphur atoms as donors [1], the diarylmercury compounds, Ar_2Hg, exhibit only feeble Lewis acidity: adducts have been isolated only from compounds with highly electronegative aryl groups, such as $(C_6F_5)_2Hg$ [2]. The arylmercury halides show intermediate behaviour: adducts of various bases with C_6F_5HgCl and C_6Cl_5HgCl have been isolated and even adducts of PhHgCl with 1,10-phenanthroline and some of its derivatives; PhHgCl(phen) is however dissociated in solution in acetone and symmetrizes to Ph_2Hg and $HgCl_2$(phen) when heated with benzene [3].

Addition of triphenylphosphine to solutions of PhHgCl in dioxane/water leads to increased conductivity [4], suggesting formation of an ionised adduct, $[PhHg \cdot PPh_3]^+Cl^-$, and adducts of alkylmercury halides with tertiary phosphines have been isolated; however these symmetrize slowly in the solid state or in solution, at rates increasing as the character of the solvent changes from benzene

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to acetone or methanol [5]. Several kinetic studies have been made of the symmetrization reaction [6], but it is not clear to what extent adducts of the type RHgX · B are precursors.

The present paper reports the results of calorimetric studies of the reaction of a series of arylmercury halides, ArHgX, with the bases 4-methylpyridine, 1,10-phenanthroline, *N,N,N',N'*-tetramethyl-1,2-diaminoethane (tmed) and some tertiary phosphines in benzene solution. The nitrogenous bases are shown to form 1 : 1 adducts in solution and thermodynamic data are reported for their formation. Phosphines lead to slow symmetrization, except for trialkylphosphines which give an instantaneous reaction, which it has not been possible to show unambiguously is symmetrization as distinct from adduct formation.

Experimental

Materials

Arylmercury halides and diarylmercury compounds, except those with pentachlorophenyl substituents, were prepared by the diazo method from the appropriate aryl amines [7]. The pentachlorophenyl compounds were prepared from hexachlorobenzene by the Grignard method [8]. All compounds were purified by crystallisation from ethanol, acetone or pyridine and purity checked by C and H analysis.

The liquid bases tributylphosphine, 4-methylpyridine and tmed were purified by distillation and the nitrogenous bases stored over anhydrous potassium carbonate. The solid bases 1,10-phenanthroline, triphenylphosphine and 1,2-bis(diphenylphosphino)ethane were purified by crystallisation from ethanol; benzene solutions of phen were dehydrated by azeotropic distillation of part of the solvent before making up to volume. Benzene for use as solvent was purified by freezing, followed by distillation and dried over calcium hydride.

Calorimetry

Calorimetric titrations were carried out in an LKB 8700-2 titration calorimeter by the technique previously described [9]. Successive increments of a

TABLE 1

THERMODYNAMIC DATA FOR FORMATION OF 1 : 1 ADDUCTS OF ArHgX WITH 4-METHYLPYRIDINE IN BENZENE SOLUTION AT 30°C (CONC. OF ArHgX IN mmol l^{-1}, K IN l mol^{-1}, ΔH^0, ΔG^0 IN kJ mol^{-1}, ΔS^0 IN J K^{-1} mol^{-1})

Ar	X	[ArHgX]	K	$-\Delta H^0$	$-\Delta G^0$	$-\Delta S^0$
C_6H_5	Br	2.0	1.8 ± 0.3	30.0 [a]	1.5 ± 0.5	
o-$CH_3C_6H_4$	Cl	13.0—17.0	1.4 ± 0.2	21.5 ± 2.8	0.9 ± 0.5	68 ± 11
p-$CH_3C_6H_4$	Cl	7.0—9.0	2.8 ± 0.4	20.7 ± 1.5	2.6 ± 0.4	60 ± 7
o-$CH_3OC_6H_4$	Cl	15.0—30.0	2.4 ± 0.2	24.2 ± 1.5	2.2 ± 0.3	72 ± 6
p-$C_2H_5OC_6H_4$	Cl	10.0—14.0	1.6 ± 0.2	27.5 ± 1.1	1.2 ± 0.4	87 ± 5
p-ClC_6H_4	Cl	7.0—14.0	2.6 ± 0.3	28.6 ± 0.9	2.4 ± 0.4	86 ± 5
o-ClC_6H_4	Cl	15.0—25.0	2.3 ± 0.2	30.1 ± 1.1	2.1 ± 0.3	92 ± 5
C_6Cl_5	Cl	1.8—2.0	3.4 ± 0.7	37.6 ± 3.7	3.1 ± 0.6	114 ± 15

[a] Arbitrary value.

benzene solution of the base, or in some instances of the pure liquid base, were added to 100 ml of a benzene solution of the mercury compound and the heat change measured after each addition of titrant. The enthalpy of reaction was obtained from the integrated, extrapolated heat of reaction and the equilibrium constant calculated at each point in the titration; the enthalpy was then adjusted by iterative refinement to give constant values of K throughout the titration. Enthalpies in Tables 1-3 are the mean of at least three titrations and uncertainties in ΔH^0 are mean deviations; uncertainties in K are the sum of mean deviations from different titrations and the average standard deviation in individual titrations; uncertainties in ΔG^0 and ΔS^0 are derived.

Results and discussion

Reaction of ArHgX with bases may lead to either adduct formation (reaction 1) or symmetrization (reaction 2):

$$\mathrm{RHgX + B \rightleftharpoons RHgX \cdot B} \qquad (1)$$

$$\mathrm{2\ RHgX + B \rightleftharpoons R_2Hg + HgX_2B} \qquad (2)$$

When the reaction is carried out as a calorimetric titration these alternatives can be distinguished by their different stoichiometries, If the adduct formation constant or symmetrization constant (K) is large, the stoichiometry can be observed directly from the ratio of the concentrations of ArHgX and base when further addition of base produces no further heat change; when K is very small the stoichiometry can be obtained from the variation of heat produced with concentration of added base at the beginning of the titration; for intermediate values of K the experimental titration data can be fitted to titration curves computed for the appropriate stoichiometry and this is confirmed by the invariance of K with changing concentration of ArHgX.

In all the systems studied the stoichiometry was found to be 1 : 1. In most instances this is conclusive evidence that the reaction taking place is adduct formation (1) not symmetrization (2), but in the case of the phosphines it is not conclusive for reasons discussed below. Further confirmation that symmetrization does not occur with the amines was obtained by repeating many of the titrations in the presence of added $\mathrm{Ar_2Hg}$; after correcting for the small heat of reaction of the base with the relatively large concentration of $\mathrm{Ar_2Hg}$, the titration curves were identical with those obtained in the absence of added $\mathrm{Ar_2Hg}$ (Fig. 1), showing that this is not a reaction product.

Data for adduct formation with 4-methylpyridine are shown in Table 1. In every case the values of K are very small and the enthalpies of reaction thus of low accuracy. Comparison of the product $K \cdot \Delta H$, which is a much more accurate parameter than either K or ΔH alone under these conditions, shows that substitution by alkoxy groups lowers the reactivity of ArHgX and substitution by chlorine raises it. In the case of $\mathrm{C_6Cl_5HgCl}$ the increased reactivity is associated with increased enthalpy of reaction and is clearly an inductive effect, but the data for the other compounds are not sufficiently accurate to show with certainty whether the changes in reactivity are due to enthalpy or entropy effects, especially as low solubility precluded the possibility of obtaining reasonably accurate data for the parent compound PhHgCl.

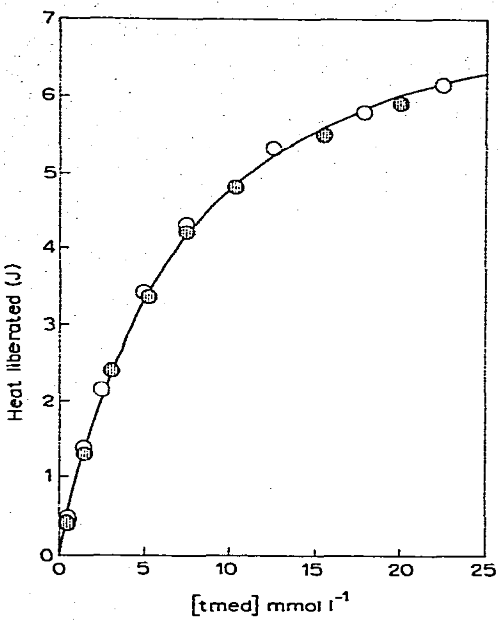

Fig. 1. Calorimetric titration of tmed with p-ClPhHgCl 2 X 10^{-3} M, ◍, and with added p-ClPh$_2$Hg 1 X 10^{-2} M, ○. Curve computed for 1 : 1 addition with $K = 170$ l mol^{-1} and $\Delta H^0 = -39.9$ kJ mol^{-1}.

The results obtained for formation of 1 : 1 adducts with the two potentially bidentate bases, phen and tmed, are shown in Table 2. Enthalpies of adduct formation are similar for phen, tmed and 4-methylpyridine, but the adducts of the bidentate bases are of much greater stability. A similar pattern has been previously observed with mercury(II) halides [10] and suggests that the bidentate bases are chelate, but that the two Hg—N bonds are each considerably weaker than the single Hg—N bond in the 4-methylpyridine adducts, or alternatively

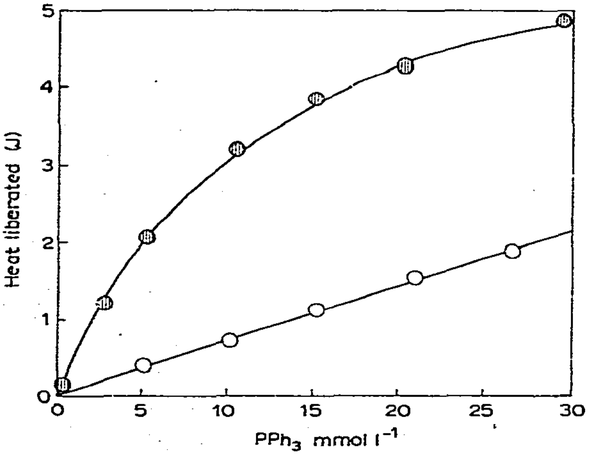

Fig. 2. Calorimetric titration of PPh$_3$ with PhHgBr 2 X 10^{-3} M, ◍, and with added Ph$_2$Hg 1.5 X 10^{-2} M, ○. Curve computed for 1 : 1 reaction with $K = 95$ l mol^{-1} and $\Delta H^0 = -33$ kJ mol^{-1}.

that when the bidentate bases form adducts with these mercury compounds one of the Hg—N bonds is much stronger than the other.

Substitution in the aryl group of ArHgX, even by five chlorine atoms, apparently has little effect on the enthalpy of formation of the phen adducts, though adduct stability is lowered by alkyl or alkoxy substitution and raised by chlorine substitution. The enthalpy of formation of PhHgBr(phen) is about 10 kJ mol^{-1} less than that of PhHgCl(phen), but the adduct of the bromide is more stable; the same pattern is repeated with tmed and with the tmed adducts of the *p*-chlorphenylmercury chloride and bromide. This suggests that the larger bromine atom has an important entropy effect, perhaps by cooperating with the added base to displace additional solvent molecules.

The limited data for adducts with tmed show a distinct inductive effect for chlorine substitution, though this is not apparent with the phen adducts. Despite this small difference there is an even closer similarity between phen and tmed in these systems than there is when these two bases react with mercury(II) halides [10] and it seems likely that in the adducts ArHgX · tmed the base is chelate and the mercury atom 4-coordinate, but with two rather weak, possibly unequal, Hg—N bonds.

Attempts were made to study the reaction of the compounds ArHgX with a wide range of other bases. Some heat was liberated when tributylamine or dimethyl sulphide were used, but the amount was too small for the calorimetric data to be analysed; with these bases there is apparently reaction, but K and probably ΔH are very small. When 2,2′-bipyridine, tetrahydrofuran, dioxan, tetrahydrothiophene or triphenylarsine was used no heat was liberated and these bases apparently do not react. In contrast to these observations tertiary phosphines liberated considerably more heat than the amines.

Since mercury(II) halides form very stable adducts $HgX_2(PR_3)_2$ with phos-

TABLE 2

THERMODYNAMIC DATA FOR FORMATION OF 1 : 1 ADDUCTS OF ArHgX WITH phen AND tmed IN BENZENE SOLUTION AT 30°C (CONC. OF ArHgX IN mmol l^{-1}, K IN l mol^{-1}, ΔH^0, ΔG^0 IN kJ mol^{-1}, ΔS^0 IN J K^{-1} mol^{-1})

Ar	X	Base	[ArHgX]	K	$-\Delta H^0$	$-\Delta G^0$	$-\Delta S^0$
C_6H_5	Br	phen	1.0—2.0	798 ± 113	20.2 ± 0.3	16.9 ± 0.4	11 ± 2
C_6H_5	Br	tmed	1.5—2.0	211 ± 71	26.3 ± 1.6	13.5 ± 1.0	42 ± 8
C_6H_5	Cl	phen	1.5—2.0	346 ± 13	30.6 ± 0.5	14.7 ± 0.1	49 ± 2
C_6H_5	Cl	tmed	1.7—2.0	137 ± 11	33.2 ± 0.5	12.4 ± 0.3	69 ± 3
o-$CH_3C_6H_4$	Cl	phen	1.0—4.0	221 ± 27	29.2 ± 1.3	13.6 ± 0.3	51 ± 5
p-$CH_3C_6H_4$	Cl	phen	3.0—5.0	298 ± 13	23.7 ± 0.6	14.4 ± 0.2	31 ± 8
p-$CH_3C_6H_4$	Cl	tmed	1.5—3.0	71 ± 4	37.0 ± 1.3	11.7 ± 0.2	83 ± 5
o-$CH_3OC_6H_4$	Cl	phen	2.5—3.5	193 ± 33	23.2 ± 2.0	13.3 ± 0.4	33 ± 8
p-$C_2H_5OC_6H_4$	Cl	phen	2.3—2.8	233 ± 6	26.1 ± 0.6	13.7 ± 0.1	41 ± 2
o-ClC_6H_4	Cl	phen	3.0—4.0	967 ± 134	29.6 ± 1.0	17.3 ± 0.4	41 ± 5
p-ClC_6H_4	Cl	phen	3.0—4.0	719 ± 65	26.7 ± 0.4	16.6 ± 0.3	33 ± 3
p-ClC_6H_4	Cl	tmed	1.5—2.5	170 ± 16	39.9 ± 1.2	12.9 ± 0.3	89 ± 5
p-ClC_6H_4	Br	tmed	2.0—2.5	228 ± 25	31.5 ± 1.6	13.7 ± 0.3	59 ± 6
C_6Cl_5	Cl	phen	1.5—2.0	>8000	28.4 ± 1.7	>22	<21
C_6Cl_5	Cl	tmed	1.8—2.0	670 ± 43	44.8 ± 1.5	16.4 ± 0.2	94 ± 6

phines, the symmetrization reaction can be expected to have different stoichiometry from that with nitrogenous bases:

$$2\ ArHgX + 2\ PR_3 \rightleftharpoons R_2Hg + HgX_2(PR_3)_2 \qquad (3)$$

In this reaction R_2Hg and $HgX_2(PR_3)_2$ are formed in equivalent amounts and the equilibrium constant K_3 is not experimentally distinct from the constant K_1 for the formation of 1 : 1 adducts, since $K_3 = K_1^2$. It is thus not possible to determine solely from equilibrium measurements whether the reaction taking place is adduct formation (1) or symmetrization (3).

When PhHgBr was titrated with triphenylphosphine, treatment of the data as for 1 : 1 adduct formation gave $\Delta H^0 = -33.0 \pm 0.8$ kJ mol^{-1} and $K_1 = 95 \pm 8$ l mol^{-1}; similarly p-$CH_3C_6H_4HgCl$ gave $\Delta H^0 = -29.0 \pm 1.6$ kJ mol^{-1} and $K_1 = 24 \pm 3$ l mol^{-1}. However in both these titrations equilibrium was reached only slowly after each addition of titrant with a half-reaction time of about one minute, suggesting that the reaction is really symmetrization, which involves bond breaking, rather than adduct formation, which involves only bond formation. Addition of a large excess of Ar_2Hg before titration suppressed the slow reaction; equilibrium was then attained instantly, but the equilibrium constant was too small for either K or ΔH to be determined (Fig. 2). Suppression of the slow reaction by added Ar_2Hg shows that this is a product of the reaction, which must therefore be symmetrization.

Titrations with 1,2-bis(diphenylphosphino)ethane (diphos) also gave exothermic reactions, slow to reach equilibrium and in this case reaction was accompanied by precipitation. The solid precipitated was isolated and shown by analysis to be $HgCl_2$(diphos), proving that symmetrization had taken place.

Attempts to confirm by NMR the formation of Ar_2Hg in solution after titration of ArHgX with phosphines were frustrated by the very low concentrations necessary. However it is possible to calculate from published data for the heats of formation of each species [11] the enthalpy of the reaction:

$$2\ PhHgCl_{(cryst)} = Ph_2Hg_{(cryst)} + HgCl_{2(cryst)} \qquad \Delta H^0 = +51\ \mathrm{kJ\ mol^{-1}}$$

In order to compare this value with that of the supposed symmetrization in solution heats of solution of PhHgCl, Ph_2Hg and $HgCl_2$ in benzene were determined by breaking ampoules containing about 0.02 g of solid compound into 100

TABLE 3

ENTHALPY OF REACTION OF ArHgX WITH PBu_3 IN BENZENE SOLUTION AT 30°C (CONC. OF ArHgX IN mmol l^{-1}, ΔH^0 IN kJ g-at Hg^{-1})

Ar	X	[ArHgX]	$-\Delta H^0$
C_6H_5	Br	0.7—1.5	69.6 ± 0.8
o-$CH_3C_6H_4$	Cl	1.0—2.0	64.8 ± 1.5
p-$CH_3C_6H_4$	Cl	1.0—2.0	66.1 ± 0.9
o-$CH_3OC_6H_4$	Cl	1.0—1.5	62.5 ± 0.9
p-$C_2H_5OC_6H_4$	Cl	1.0—2.0	66.5 ± 1.3
o-ClC_6H_4	Cl	1.3—2.0	70.5 ± 0.3
p-ClC_6H_4	Cl	1.5—2.5	68.6 ± 0.3
C_6Cl_5	Cl	1.8—2.0	67.1 ± 0.2

ml of benzene. Because of the very low solubility of PhHgCl the solutions obtained from this compound were nearly saturated; to provide a check against possible errors arising from this, data were also obtained for the more freely soluble p-ClPhHgCl and p-ClPh$_2$Hg. The enthalpies of solution found were as follows (kJ mol^{-1}): HgCl$_2$, —1 ± 2; PhHgCl, +8 ± 2; p-ClPhHgCl +5 ± 2; Ph$_2$Hg, +8 ± 3; p-ClPh$_2$Hg, +6 ± 3. These results were then combined with the previously published data for the reaction of HgCl$_2$ with PPh$_3$ in benzene solution [1] to give the expected enthalpy of symmetrization of PhHgCl in benzene (ΔH^0 in kJ mol^{-1}):

$$2\,\mathrm{PhHgCl}_{(c)} = \mathrm{Ph_2Hg}_{(c)} + \mathrm{HgCl}_{2(c)} \qquad \Delta H^0 = +51$$

$$2\,\mathrm{PhHgCl}_{(\mathrm{benz})} = 2\,\mathrm{PhHgCl}_{(c)} \qquad \Delta H^0 = -16$$

$$\mathrm{Ph_2Hg}_{(c)} = \mathrm{Ph_2Hg}_{(\mathrm{benz})} \qquad \Delta H^0 = +8$$

$$\mathrm{HgCl}_{2(c)} = \mathrm{HgCl}_{2(\mathrm{benz})} \qquad \Delta H^0 = -1$$

$$\mathrm{HgCl}_{2(\mathrm{benz})} + 2\,\mathrm{PPh}_{3(\mathrm{benz})} = \mathrm{HgCl_2(PPh_3)}_{2(\mathrm{benz})} \qquad \Delta H^0 = -108$$

$$2\,\mathrm{PPh}_{3(\mathrm{benz})} + 2\,\mathrm{PhHgCl}_{(\mathrm{benz})} = \mathrm{Ph_2Hg}_{(\mathrm{benz})} + \mathrm{HgCl_2(PPh_3)}_{2(\mathrm{benz})} \qquad \Delta H^0 = -66$$

The calculated enthalpy of symmetrization of PhHgCl in benzene solution (—33 kJ mol^{-1}) compares remarkably well with the value obtained by calorimetric titration of PhHgCl with PPh$_3$ and provides further confirmation that this reaction is symmetrization.

When the compounds ArHgX were titrated with tributylphosphine equilibrium was reached immediately after the addition of each portion of titrant, suggesting addition rather than symmetrization. Treatment of the data as for 1 : 1 adduct formation gave very large equilibrium constants ($K_1 > 10^4$ l mol^{-1}) and enthalpies of reaction of about —67 kJ mol^{-1}, little affected by substitution in the arylmercury compound (Table 3).

Addition of Ar$_2$Hg before starting the titration produced no change in either K or ΔH^0, but this is not conclusive evidence against symmetrization as K is very large and any change produced by accessible concentrations of Ar$_2$Hg may not be observable. Combination of the enthalpy data for symmetrization in the solid state and heats of solution and of reaction of HgCl$_2$ with PBu$_3$ to form HgCl$_2$(PBu$_3$)$_2$ in benzene solution [1] (—177 kJ g.-at Hg^{-1}) gives the expected enthalpy of symmetrization of PhHgCl by PBu$_3$ in benzene solution:

$$2\,\mathrm{PhHgCl}_{(\mathrm{benz})} = \mathrm{Ph_2Hg}_{(\mathrm{benz})} + \mathrm{HgCl_2(PBu_3)}_{2(\mathrm{benz})} \qquad \Delta H^0 = -135 \text{ kJ mol}^{-1}$$

this also is very close to the observed enthalpy of reaction of —66 kJ g.-at Hg^{-1} when the reaction is carried out as a calorimetric titration, giving strong support to the proposition that the reaction of ArHgX with PBu$_3$ leads to symmetrization, as it does with PPh$_3$, and the reaction with PBu$_3$ is much more rapid.

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