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STABILITY AND BOND STRENGTH IN ADDUCTS OF MERCURY(II) HALIDES WITH TRANSITION METAL CARBONYL DERIVATIVES

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Summary

Thermodynamic data have been obtained calorimetrically for the reaction of a range of Group VI transition metal carbonyl derivatives with mercury(II) halides in 1,2-dichloroethane solution. The results show that the enthalpies of adduct formation are more negative when the transition metal atom has a lower electronegativity, due to large size or coordination of arenes or phosphines. Enthalpies of adduct formation are slightly more negative than those of adducts of mercury(II) halides with conventional Lewis bases, suggesting that the mercury—metal bonds formed are at least as strong as equivalent Hg—N or Hg—P bonds. The influence of entropy effects on adduct stabilities is shown by the high stabilities of chromium compounds, despite generally less negative enthalpies of formation.

Introduction

It has long been known that some transition metal carbonyl derivatives, such as Vaska's compound $IrCl(CO)(PPh_3)_2$, can undergo oxidative addition reactions, in which the metal atom increases its coordination number [1,2]. Strong Lewis acids, such as boron trifluoride, also react with these compounds forming 1/1 or 1/2 adducts, in which the metal atom behaves as a Lewis base [3]. Similar adducts have been reported between a range of arenemetal carbonyls (chromium, molybdenum, tungsten, iron) and mercury(II) or tin(IV) halides [4]: the crystal structure of the closely related cyclopentadienylcobalt dicarbonyl/mercury(II) chloride adduct confirms the presence of metal—mercury bonds [5], comparable in length to those observed [6] in mercury—bis(tetracarbonylcobalt).

Usually when a transition metal undergoes reactions which lead to an increased coordination number the metal behaves as a Lewis acid and the added species is a conventional Lewis base with, for example, nitrogen or oxygen as the donor atom. Thermodynamic data have been previously reported for the reactions of many such Lewis bases with mercury(II) halides in benzene solution [7] and these observations have now been extended to systems in which mercury(II) halides as Lewis acids react with transition metal carbonyl derivatives as bases.

This paper reports enthalpy and free energy data for the reactions of mercury(II) halides with a range of derivatives of chromium, molybdenum and tungsten carbonyls. Data have been obtained calorimetrically, using, 1,2-dichloroethane as solvent in order to obtain adequate solubilities. In most of the systems studied the adducts formed were of fairly high stability and enthalpies of adduct formation were comparable to those for adducts of mercury(II) halides with conventional Lewis bases.

Experimental

Materials

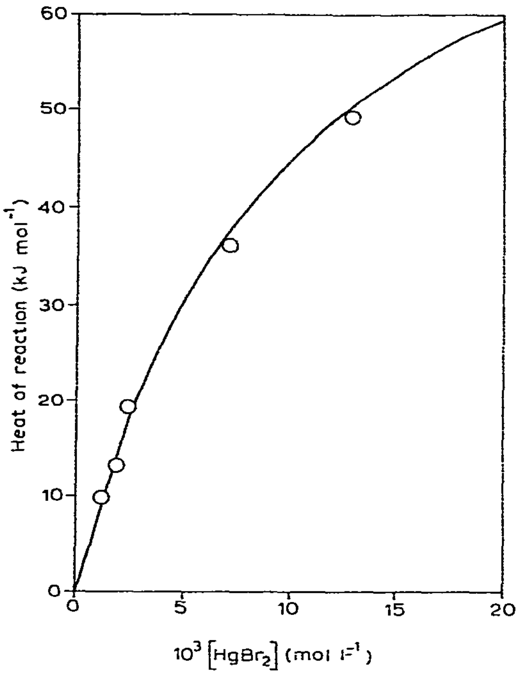
Mesitylenetricarbonylchromium, $MesCr(CO)_3$, $MesMo(CO)_3$, $MesW(CO)_3$, methylbenzoatetricarbonylchromium, $MbCr(CO)_3$, methyl-*p*-aminobenzoatetricarbonylchromium, $MabCr(CO)_3$, 2,2′-bipyridinetetracarbonylmolybdenum, $BipyMo(CO)_4$, bis-1,2-diphenylphosphinoethanetetracarbonylchromium, $DiphosCr(CO)_4$, $DiphosMo(CO)_4$, $DiphosW(CO)_4$, $Diphos_2Mo(CO)_2$, triphenylphosphinetetracarbonyliron $Ph_3PFe(CO)_4$, were prepared and purified according to methods in the literature [8-12] and their purity checked by carbon and hydrogen analysis. Mercury(II) halides were purified by crystallisation from ethanol. 1,2-Dichloroethane for use as solvent was shaken with anhydrous potassium carbonate to remove some water and traces of hydrogen chloride, then distilled and stored over anhydrous calcium chloride.

Calorimetry

Numerous simultaneous determinations of enthalpy and free energy of addition reactions have been carried out in this laboratory by a standard calorimetric titration technique [13]; in this method the maximum volume of titrant which can be added to 100 ml of reactant solution is about 5 ml, so that even when the adduct formation constant is very large the concentration of the titrant solution must be at least twenty times as great as that of the reactant and if the formation constant is small much higher concentrations of titrant solution must be used. In the present system it was not possible to obtain such concentrated solutions of either reactant and calorimetric titration data had to be obtained by more laborious methods. Two closely similar techniques were used:

1. A small volume, about 0.5 ml, of a solution of the transition metal compound was enclosed in an ampoule which was broken into the mercury halide solution after equilibration. A calorimetric titration curve was assembled by repeatedly breaking ampoules into mercury halide solutions of different concentrations. Fig. 1 shows data obtained in this way for the reaction of $MesMo(CO)_3$ with mercury(II) bromide.

2. An alternative technique was developed in which a small volume of a pre-equilibrated solution of the transition metal compound was added to the mercury halide solution from a burette. The advantage of this method was that larger volumes of the solution of the transition metal compound could be added



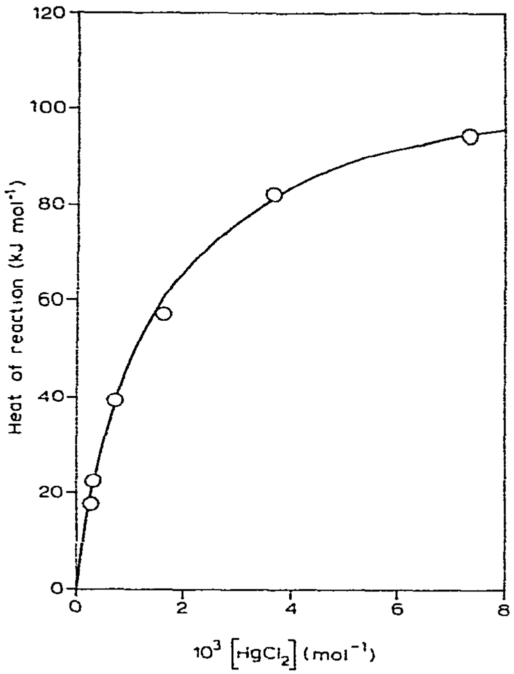


Fig. 1. Heat of reaction of approximately 4 × 10^{-4} *M* MesMo(CO)$_3$ with HgBr$_2$. Ampoule technique. Experimental points and curve calculated for $K = 100$ and $\Delta H = -90$ kJ mol^{-1}.

Fig. 2. Heat of reaction of 1.54 × 10^{-4} *M* MesW(CO)$_3$ with HgCl$_2$. Burette technique. Experimental points and curve calculated for $K = 800$ and $\Delta H = -110$ kJ mol^{-1}.

and the small variation in added volume, inevitable in the ampoule technique, but readily allowed for in the calculations, could be avoided. Fig. 2 shows results obtained by this method for the reaction of MesW(CO)$_3$ with mercury(II) chloride.

All calorimetric measurements were made in a LKB 8700 calorimeter at 30.0 ± 0.1° C, each experiment being calibrated internally by electrical heating. Control experiments were carried out to determine any correction necessary for heat produced by addition of solvent alone. Where reactions went to completion or nearly so, heats of reaction were reproducible within ±2% for different excess concentrations of mercury halides, but as adduct stability decreased the accuracy of enthalpy data necessarily also became less. The rather awkward technique used gave less accurate results than have been obtained by straightforward calorimetric titrimetry, but consideration of all sources of error leads us to believe that the uncertainty in ΔH is rarely greater than ±10%. Uncertainties in adduct formation constant are about 15% in the range $10 < K < 1000$, but are larger for extreme values of *K*.

Results and discussion

Thermodyanmic data obtained for addition of the transition metal carbonyl derivatives to mercury(II) halides are summarised in Table 1, in which

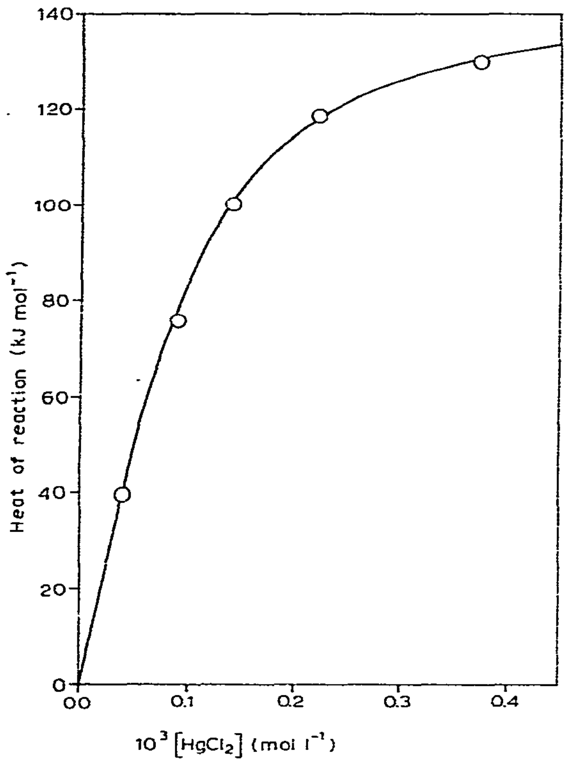


Fig. 3. Heat of reaction of 8.6×10^{-5} *M* diphosW(CO)$_4$ with HgCl$_2$. Experimental points and curve calculated for $K = 3 \times 10^4$ and $\Delta H = -145$ kJ mol^{-1}.

TABLE 1

THERMODYNAMIC DATA FOR ADDITION OF MERCURY(II) HALIDES TO METAL CARBONYL DERIVATIVES IN 1,2-DICHLOROETHANE SOLUTION AT 30°C

Carbonyl	Halide	K (l mol^{-1})	$-\Delta H$ (kJ mol^{-1})	$-\Delta G$ (kJ mol^{-1})	$-\Delta S$ (J K^{-1} mol^{-1})
MesW(CO)$_3$	HgCl$_2$	800 ± 170	105 ± 5	16.9 ± 0.5	290 ± 17
MesW(CO)$_3$	HgBr$_2$	330 ± 50	110 ± 10	14.6 ± 0.4	315 ± 32
MesMo(CO)$_3$	HgBr$_2$	100 ± 15	90 ± 10	11.6 ± 0.5	260 ± 32
MesCr(CO)$_3$	HgCl$_2$	2×10^3	9 ± 3	c. 19	—33 ± 10
MbCr(CO)$_3$	HgCl$_2$	$>10^3$	5 ± 3	>17	<—30
MabCr(CO)$_3$	HgCl$_2$	$>10^3$	5 ± 3	>17	<—30
BipyMo(CO)$_4$	HgCl$_2$	$>10^3$	14 ± 3	>17	< 0
DiphosW(CO)$_4$	HgCl$_2$	3×10^4	145 ± 10	c. 27	357 ± 40
DiphosW(CO)$_4$	HgBr$_2$	c. 10^5	140 ± 10	c. 29	366 ± 40
Diphos$_2$Mo(CO)$_2$	HgCl$_2$	c. 10^5	80 ± 5	c. 29	169 ± 24
Diphos$_2$Mo(CO)$_2$	HgBr$_2$	c. 10^5	90 ± 5	c. 29	202 ± 24
DiphosMo(CO)$_4$	HgCl$_2$	—	13 ± 2 [a]	—	—
DiphosCr(CO)$_4$	HgCl$_2$	—	24 ± 3 [a]	—	—

[a] Independent of [HgCl$_2$] if ≠ 0.

attempts are made to estimate the uncertainties of the results. Among the arenemetal carbonyls the largest enthalpies of adduct formation were observed with $MesW(CO)_3$. Precipitation of the adduct of $MesMo(CO)_3$ and $HgCl_2$ frustrated measurement of adduct formation data in this case, but the molybdenum compound gave an adduct with $HgBr_2$ of only slightly lower stability than that of the tungsten compound.

The enthalpy of addition of $MesCr(CO)_3$ and $HgCl_2$ was much lower, making accurate determination of the formation constant very difficult; the stability of this adduct is however clearly higher than those of the molybdenum and tungsten compounds, despite the much lower enthalpy of formation. Replacement of mesitylene by methylbenzoate or *p*-aminobenzoate in the chromium compound led to even lower enthalpies of adduct formation, though adduct stability remained high.

The greater enthalpies of formation of adducts with molybdenum or tungsten compounds compared with chromium may be related to greater availability of non-bonding electrons of the larger metal atoms; the increased stability of the adducts of chromium compounds, in spite of lower enthalpies of formation, can then be seen as an entropy effect, possibly arising from displacement of larger numbers of solvent molecules due to the more compact adduct structure. The still lower enthalpies of formation of adducts of the benzoic acid derivatives appears to be an inductive effect transmitted from the aryl ring to the donor chromium atom.

$BipyMo(CO)_4$ reacted with mercury(II) chloride in a rather similar manner to the chromium compounds: a 1/1 adduct was formed of high stability, but with a comparatively low enthalpy of reaction. As coordination of N-donors could be expected to raise the electronegativity of the metal atom compared with the arene complexes, this is consistent with a high transition metal—mercury bond strength arising when the metal atom has a low electronegativity.

Attempts were also made to determine the heats of reaction of the compounds $MesM(CO)_3$ with phenylmercury chloride, aluminium chloride, cadmium iodide and tin(IV) chloride, but in no case were measurable amounts of heat produced; in the last case, however, the large heat of dilution of tin(IV) chloride, even from already dilute solutions, would have obscured any heat of reaction with the metal carbonyl compounds if the enthalpy of reaction were less than about 20 kJ mol^{-1}. Since stable adducts of these metal compounds with tin(IV) have been isolated [4], it is interesting to note that this upper limit of about 20 kJ mol^{-1} for their enthalpies of formation is considerably less than those of the mercury(II) halide adducts.

The adducts with 1,2-bis(diphenylphosphino)ethane were particularly interesting. Adducts of the types $diphosM(CO)_4 \cdot HgCl_2$ and $diphos_2M(CO)_2 \cdot 2\,HgX_2$ have been isolated [4]. In solution in 1,2-dichloroethane $diphos_2Mo(CO)_2$ and $diphosW(CO)_4$ both formed 1/1 adducts of high stability. Conductivity studies showed that only slight ionisation accompanied formation of these adducts; for example in 10^{-3} molar solution a value of $\Lambda_M = 0.54$ ohm^{-1} cm^{-1} was obtained for $diphos_2Mo(CO)_2$, 1.29 for $HgBr_2$ and 3.8 for the 1/1 adduct, values of Λ_M in the range 16-22 ohm^{-1} cm^{-1} have been reported for 1/1 electrolytes in 1,2-dichloroethane solution [14,15].

$DiphosMo(CO)_4$ and $diphosCr(CO)_4$ both behaved in a similar curious manner: a small heat of reaction with mercury(II) chloride was observed, unaffected by the mercury(II) chloride concentration over a very wide range of concentrations from Hg $\ll$ M to Hg $\gg$ M. It seems probable in these cases that the heat observed is not associated with adduct formation, but with some other reaction, perhaps loss of carbon monoxide, which is catalysed by the mercury(II) chloride. A somewhat similar phenomenon was observed when attempts were made to obtain data for adduct formation with $Ph_3PFe(CO)_4$. In this case equilibrium was achieved only slowly and the reaction is clearly complex. Here too 1/1 adducts have been isolated and presumably immediate precipitation of the adducts from more concentrated solutions prevents the slow reaction from taking place; it was not found possible to identify the products of this slow reaction.

The results reported here show that in favourable cases, where the transition metal atom has low electonegativity conferred by large size and/or coordination to arenes or phosphines, adducts with mercury(II) halides can be formed as stable as those formed by most conventional Lewis bases. Indeed the enthalpies of formation of 80-140 kJ mol^{-1} are amongst the largest reported for Lewis acid—base systems.

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