Thermochemistry of Dichlorobis(triphenylphosphine oxide)-zinc(II), -cadmium(II), and -mercury(II)

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The standard enthalpy change ($\Delta H_R^\ominus$) for the reaction $MCl_2(s) + 2PPh_3O(s) \longrightarrow [MCl_2(PPh_3O)_2](s)$ (M = Zn, Cd, or Hg) has been determined by solution calorimetry as −51.1 ± 2.2 (Zn), −16.3 ± 0.5 (Cd), and −12.3 ± 0.6 kJ mol^{-1} (Hg) respectively. From the standard enthalpies of formation ($\Delta H_f^\ominus$) of the crystalline anhydrous metal chlorides and the ligand, the $\Delta H_f^\ominus$ values of the zinc, cadmium, and mercury adducts are −586.6 ± 50, −528.3 ± 50, and −357.7 ± 50 kJ mol^{-1}. The standard enthalpy change due to the sublimation of ligand (−66.0 kJ mol^{-1}) has also been determined. Since the adducts do not sublime, the possibility of evaluating the enthalpy of the metal–oxygen bonds is discussed.

THE adducts of zinc-, cadmium-, and mercury-(II) halides with phosphine oxides have been known since the last century;[1] $ZnI_2 \cdot 2PEt_3O$ was reported in 1861. A recent review [2] quoted many publications concerned with the structural characterization of these complexes, based mainly on variations of the P–O stretching vibration of the free and complexed ligand [3] [Δν(PO)]. Thus, the shift in the P–O stretching frequency caused by adduct formation, as a consequence of the weakening of this bond, has been interpreted as a measure of the bond strength. This assumption has been criticized, with the suggestion that it is valid ' only if the acceptor molecules are compared under very similar conditions '.[4,5]

The literature contains many attempts to correlate Δν(PO) and bond strength, the latter being measured by the enthalpy of formation of adducts in solution, using media of low solvating power.[6-8] However, none of them gives a really satisfactory correlation.[9-12] An early reference [13] shows that there is some correlation between Δν(PO) and the order of acidity of metal halides given by another worker.[14] The relationship between this correlation and that between Δν and the bond strength is not clear.

The lack of thermochemical data makes it difficult to set out the energetic problem involved in the formation of the adducts. In our laboratory we have elaborated a plan to obtain some necessary thermochemical data for the reaction between phosphine oxides and zinc-, cadmium-, and mercury-(II) halides. Here we report such a study of the reactions between triphenylphosphine oxide and the above metal chlorides.

EXPERIMENTAL

Materials and Complexes.—Analytical grade materials were used. Triphenylphosphine oxide was prepared by oxidation of triphenylphosphine [15] with bromine and subsequent hydrolysis with aqueous sodium hydroxide. The product, m.p. 156—157 °C, was recrystallized from ethyl acetate. Anhydrous zinc(II) chloride was prepared by the reaction of hydrogen chloride (gas) with metallic zinc in anhydrous diethyl ether.[16] The compound $CdCl_2 \cdot 2.5H_2O$ was dried by stirring with acetyl chloride.[17] After filtration and drying *in vacuo* the anhydrous salt was obtained. Anhydrous mercury(II) chloride (E. Merck) was used without further purification. The complexes of PPh_3O with $ZnCl_2$, $CdCl_2$, and $HgCl_2$ were prepared as described in the literature [13,18,19] and recrystallized from anhydrous dioxan (m.p. 230—231 and 172—173 °C), and from 1,2-dichloroethane (m.p. 125—126 °C), respectively. Metal

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analysis for the adducts and the anhydrous salts gave very satisfactory results.

The calorimetric solvents were selected for their ability to dissolve the anhydrous salts, the ligand, and the adducts. Before preparing the ampoules, the salts, the ligand, and adducts were rigorously dried *in vacuo* and a dry-box was used for air-sensitive compounds.

TABLE 1

Standard enthalpies (kJ mol^{-1}) for equations (2)—(4) and the standard enthalpies of the reaction between the ligand and the respective halides in the solid state

Compound	Calorimetric solvent	$\Delta H_1^\ominus$	$\Delta H_2^\ominus$	$\Delta H_3^\ominus$	$\Delta H_R^\ominus$
$[ZnCl_2(PPh_3O)_2]$	Dioxan	-40.7 ± 0.8 (6) *	28.0 ± 0.8 (6)	38.4 ± 0.6 (7)	-51.1 ± 2.2
$[CdCl_2(PPh_3O)_2]$	EtOH	-7.2 ± 0.1 (5)	31.2 ± 0.2 (6)	40.3 ± 0.2 (6)	-16.3 ± 0.5
$[HgCl_2(PPh_3O)_2]$	Dioxan	-18.0 ± 0.4 (5)	33.2 ± 0.2 (6)	27.42 ± 0.04 (5)	-12.3 ± 0.6
	CH_2ClCH_2Cl	13.4 ± 0.3 (8)	30.4 ± 0.6 (6)	56.4 ± 0.5 (8)	-12.6 ± 1.4

* The number of runs is given in parentheses.

Calorimetric Measurements.—The LKB 8700-1 precision calorimetric system was used for all the solution reactions. A high (1 MΩ) input impedance strip-chart recorder (Servogor S) was coupled to the null voltmeter (Hewlett–Packard 419A) of the calorimeter.[20] The system for temperature measurements included a thermistor in a Wheatstone bridge, a null voltmeter, and the recorder, and enabled us to verify that the temperature change is directly proportional to the recorder-pen displacement. Electrical calibration inputs, through the resistance of the heater of the calorimeter, enabled us to calibrate the chart directly in energy units (J/mm).

Ampoules containing 1—150 mg of the solid reactant were broken into the glass reaction vessel (100 cm^3) charged with a suitable calorimetric solvent. The measurements were performed at 25.04 ± 0.02 °C. A check on the accuracy of the calorimeter was carried out by determining the heat of dissolution of tris(hydroxymethylamino)methane in 0.1 mol dm^{-3} hydrochloric acid. The result (-29.69 ± 0.09 kJ mol^{-1}) is in agreement with the value recommended by I.U.P.A.C.[21] (-29.763 ± 0.003 kJ mol^{-1}). The uncertainty interval is twice the standard deviation of the mean.

Other Measurements.—Infrared spectra were recorded for samples in Nujol mulls between sodium chloride windows, using a Perkin-Elmer model 180 spectrophotometer, previously calibrated with indene. The mass spectrum of $[HgCl_2(PPh_3O)_2]$ was recorded on a Varian-Mat 311A, and of the other compounds on a Finningan 1015 S/L instrument. The enthalpy of fusion and the heat capacity of the ligand were determined in a Perkin-Elmer DSC 2B differential scanning calorimeter. Thermogravimetric determinations were made using a Perkin-Elmer TGS-1 thermobalance.

RESULTS

The P–O stretching frequencies ν(PO) for the free and complexed ligand, and the difference between them Δν(PO), shown in parentheses, are: PPh_3O 1 188; $[ZnCl_2(PPh_3O)_2]$ 1 150 (38); $[CdCl_2(PPh_3O)_2]$ 1 195 and 1 177 (2); and $[HgCl_2(PPh_3O)_2]$ 1 157 cm^{-1} (31 cm^{-1}). The value Δν(PO) for the cadmium adduct was calculated by using the median position of the doublet.[3] The literature values of Δν(PO) are 33, 14, and 25 cm^{-1} for the zinc,[22] cadmium,[13] and mercury compounds,[19] respectively.

The thermograms of the zinc and mercury adducts presented a continuous loss of mass above the melting point, up to complete vaporization, which is at 400 °C for the zinc and at 275 °C for the mercury adduct. The cadmium adduct lost mass between the melting point and 320 °C, followed by a smooth plateau to complete vaporization at 540 °C, at which point nearly all the ligand had been lost.

Several mass spectra of the adducts were obtained below and above the fusion point. The results are listed as the compound, the temperature used, and the mass (fragmentation in parentheses). For comparison the values for PPh_3O are also listed. PPh_3O, 35 °C: *m/e* 278(PPh_3O), 201(PPh_2O), 185(PPh_2), 171 and 173 (?), 154(Ph_2), 124(PPhO), 93(OPh), and 78(Ph). $[ZnCl_2(PPh_3O)_2]$, 245 °C: *m/e* 479[$ZnCl_2(PPh_3O)$], 378[$ZnCl(PPh_3O)$], 343[$Zn(PPh_3O)$], 278(PPh_3O), 262(PPh_3), 201(PPh_2O), 185(PPh_2), 171 and 173(?), 154(Ph_2), 136($ZnCl_2$), 124(PPhO), 108(PPh), 93(OPh), and 77(Ph). $[CdCl_2(PPh_3O)_2]$, 120 and 190 °C: in both cases the peaks confirm the presence of free ligand only. $[HgCl_2(PPh_3O)]$, 90 and 132 °C: *m/e* 278(PPh_3O), 271($HgCl_2$), 201(PPhO), 185(PPh_2), 170(OPh_2), 154(Ph_2), 124(PPhO), 108(PPh), 93(OPh), and 77(Ph).

The standard enthalpy of formation ($\Delta H_f^\ominus$) of the adducts can be determined from the enthalpy of formation of the metal chlorides MCl_2 (M = Zn, Cd, or Hg), the enthalpy of formation of the ligand, and the enthalpy of the subsequent solid-state reaction (1) ($\Delta H_R^\ominus$). $\Delta H_R^\ominus$ can be derived by

$$MCl_2(s) + 2PPh_3O(s) \longrightarrow [MCl_2(PPh_3O)_2](s) \qquad (1)$$

applying the Hess law to the sequence (2)—(5) in a suitable calorimetric solvent. The results obtained from equations

$$MCl_2(s) + \text{calorimetric solvent} \xrightarrow{\Delta H_1^\ominus} \text{solution (A)} \qquad (2)$$

$$\text{solution (A)} + 2PPh_3O(s) \xrightarrow{\Delta H_2^\ominus} \text{solution (B)} \qquad (3)$$

$$[MCl_2(PPh_3O)_2](s) + \text{calorimetric solvent} \xrightarrow{\Delta H_3^\ominus} \text{solution (C)} \qquad (4)$$

$$\text{solution (B)} \xrightarrow{\Delta H_4^\ominus} \text{solution (C)} \qquad (5)$$

(2)—(4) and $\Delta H_R^\ominus$ are summarised in Table 1. Table 2 lists $\Delta H_f^\ominus$ of the adducts. $\Delta H_5^\ominus$ for the ligand in dioxan,

$$PPh_3O(s) + \text{calorimetric solvent} \xrightarrow{\Delta H_5^\ominus} \text{solution (D)} \qquad (6)$$

ethanol, or 1,2-dichloroethane was determined as 16.30 ± 0.04, 16.1 ± 0.1, and 16.2 ± 0.4 kJ mol^{-1} respectively;

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[20] LKB 8700 Precision Calorimetry System, Instruction Manual and Application, Note MLB/an-31, LKB-Produkter AB, Bromma 1, Sweden.

[21] E. F. G. Henrigton, *Pure Appl. Chem.*, 1974, **40**, 391.

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in each case at least six runs were employed. $\Delta H_D^\ominus$ and $\Delta H_L^\ominus$ were calculated for equations (7) and (8) and have been used to compare and systematize data for adducts which do not sublime without decomposition.[23]

$$[MCl_2(PPh_3O)_2](s) \xrightarrow{\Delta H_D^\ominus} MCl_2(s) + 2PPh_3O(g) \quad (7)$$

$$[MCl_2(PPh_3O)_2](s) \xrightarrow{\Delta H_L^\ominus} MCl_2(g) + 2PPh_3O(g) \quad (8)$$

The standard enthalpy of sublimation of each metal chloride was obtained from the literature (Table 2) and the standard enthalpy of sublimation of PPh_3O from the relation $\Delta H_{sub}^\ominus$ (298 K) = $\Delta H_{fus}^\ominus$ (298 K) + $\Delta H_{vap}^\ominus$ (298 K). $\Delta H_{fus}^\ominus$ (298 K) was calculated by using the expression $\Delta H_{fus}^\ominus$ (298 K) = $\Delta H_{fus}^\ominus$ (429 K) + $\int_{298}^{429} C_p(s)dT - \int_{298}^{429} C_p(l)dT$, where $\Delta H_{fus}^\ominus$ (429 K) = 23.8 ± 0.4 kJ mol^{-1}, $C_p(s) = (4.7 \pm 0.1) \times 10^2$ J K^{-1} mol^{-1}, and $C_p(fus) = 5.84 \times 10^2$ J K^{-1} mol^{-1}. $\Delta H_{vap}^\ominus$ (298 K) was obtained using the Riedel–Planck–Miller equation, given by Reid and Sherwood.[24] The critical parameters were calculated from the equations of Meissner and Redding, given by Janz.[25]

TABLE 2

Summary of thermochemical data (kJ mol^{-1}) for the ligand, halides, and adducts

Compound	$\Delta H_f^\ominus$	$\Delta H_{sub}^\ominus$	$\Delta H_D^\ominus$	$\Delta H_L^\ominus$
$ZnCl_2$ (s)	−415.05 [a]	148.9 [a]		
$CdCl_2$ (s)	−391.50 [a]	181.2 [b]		
$HgCl_2$ (s)	−224.3 [a]	83.3 [c]		
PPh_3O (s)	−60.2 ± 25.1 [d]	66.0		
$[ZnCl_2(PPh_3O)_2]$ (s)	−586.6 ± 50		183	332
$[CdCl_2(PPh_3O)_2]$ (s)	−528.3 ± 50		148	329
$[HgCl_2(PPh_3O)_2]$ (s)	−357.7 ± 50		144	227

[a] D. D. Wagman, W. H. Evans, V. B. Parker, I. Halow, S. M. Bailey, and R. H. Schumm, 'Selected Values of Thermodynamic Properties,' Technical Note 270–3, National Bureau of Standards, Washington, D.C., 1968. [b] F. J. Keneshea and D. D. Cubicciotti, *J. Chem. Phys.*, 1964, **40**, 1778. [c] O. Kubaschewski, E. Ll. Evans, and C. B. Alcock, 'Metallurgical Thermochemistry,' Internat. Ser. Monographs Metal Physics and Phys. Metallurgy, vol. 1, 4th edn., Pergamon, London, 1967. [d] Ref. 26.

On the other hand, Bedford and Mortimer[26,27] estimated a value of 80.9 kJ mol^{-1} for the standard enthalpy of sublimation, but they did not discuss the method of calculation.

DISCUSSION

The mass spectra of the adducts did not show the presence of a parent ion; the compounds probably do not exist in significant amounts in the gas phase. These results were confirmed by thermogravimetry which shows that the adducts suffer decomposition without sublimation, leaving an inhomogeneous solid phase.

The $\Delta H_D^\ominus$ and $\Delta H_L^\ominus$ values (Table 2), which are positive, decrease from zinc to mercury and are not correlated with $\Delta\nu$(PO) values.

The enthalpies of metal–oxygen bonds, $\Delta H^\ominus$(M–O), may be calculated through the following thermodynamic cycle, where $\Delta H^\ominus(M-O) = \frac{1}{2}\Delta H_B^\ominus = \frac{1}{2}[-\Delta H_R^\ominus + \Delta H_{sub}^\ominus (MCl_2) + 2\Delta H_{sub}^\ominus (PPh_3O) - \Delta H_{sub}^\ominus (\text{adduct})]$. The last term, the enthalpy of sublimation of the adduct, cannot be determined because, when heated, the adduct decomposes as shown by thermogravimetry and mass spectrometry. However, the enthalpy of metal–oxygen bonds can be evaluated by considering $\Delta H^\ominus(M-O) = A - \frac{1}{2}\Delta H_{sub}^\ominus$ (adduct), from which A = 166, 165, and 114 kJ mol^{-1} for zinc, cadmium, and mercury, respectively. These values show that the bond enthalpies follow the sequence Zn ≃ Cd > Hg.

$$\begin{tikzcd}
{[MCl_2(PPh_3O)_2](g)} \arrow[r, "\Delta H_B^\ominus"] & MCl_2(g) & + & PPh_3O(g) \\
{[MCl_2(PPh_3O)_2](s)} \arrow[u, "\Delta H_{sub}^\ominus(\text{adduct})"'] & MCl_2(s) \arrow[l, "\Delta H_R^\ominus"'] \arrow[u, "\Delta H_{sub}^\ominus(MCl_2)"'] & + & PPh_3O(s) \arrow[u, "\Delta H_{sub}^\ominus(PPh_3O)"']
\end{tikzcd}$$

In an attempt to evaluate the enthalpy of the metal–oxygen bond the enthalpy of the adduct was considered as approximately equal to the enthalpy of sublimation of 1 mol of ligand. This behaviour was observed for the thiourea adducts and values of $\Delta H^\ominus$(M–S) = 117, 127, and 92 kJ mol^{-1} were determined for zinc, cadmium, and mercury, respectively.[28] Our compounds gave values of $\Delta H^\ominus$(M–O) = 133, 132, and 81 kJ mol^{-1} for the same sequence of metals. Inspection of these values shows that for zinc and cadmium the metal–ligand bond enthalpies are higher for the triphenylphosphine oxide adducts, whereas for mercury the value is higher for the thiourea adduct. This difference is in agreement with the preference of zinc and cadmium for bonding with oxygen, whereas mercury prefers to bond with sulphur.[29]

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