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Thermochemistry of adducts of triphenyl derivatives of N, P and As with arsenic trihalides

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Abstract

The complexes $\text{AsX}_3 \cdot n\text{L}$ (where L is triphenylamine (NPh_3), triphenylphosphine (PPh_3) or triphenylarsine (AsPh_3); $n = 1, 3/2, 2$ or 3 , and X is Cl, Br or I) were synthesized and characterized by melting points, elemental analysis, thermal studies, mass spectra and IR spectroscopy. From the enthalpies of dissolution in 25 or 50% diethylether in acetone, 10% ethanolamine in acetone or 20% cyclohexane in acetone, and using the appropriate thermochemical cycles, the following thermochemical parameters for the adducts have been determined: the standard enthalpies for the Lewis acid/base reaction ($\Delta_r H^\ominus$), the standard enthalpies of formation ($\Delta_f H^\ominus$), the standard enthalpies of decomposition ($\Delta_D H^\ominus$), the lattice standard enthalpies ($\Delta_M H^\ominus$) and the standard enthalpies of the Lewis acid/base reactions in the gaseous phase ($\Delta_r H^\ominus(\text{g})$). The mean standard enthalpies of arsenic–group-V element bonds have been estimated.

Keywords: Enthalpies of As–N, As–P and As–P bonds; Solution heats of arsenic trihalide adducts; Thermal studies of arsenic trihalides adducts; Thermochemical parameters of arsenic trihalide adducts; Thermochemistry of arsenic trihalides adducts

1. Introduction

The synthesis of several complexes of triphenyl derivatives of N, P and As with transition element ions is found in the literature [1–3]. However, complexes of these ligands with arsenic trihalides are not found. No information about the enthalpy of the arsenic–donor-atom bonds in these kinds of compounds is available in the literature. Adducts of arsenic trihalides and triphenylamine, triphenylphosphine or triphenylarsine were synthesized with the purpose of obtaining the enthalpies involved in the

formation of the adducts, and to establish correlations between the bond energies and the position of the donor atom of the ligand in the Periodic Table. The expected ligand stability sequence for AsI_3 is $\text{N} < \text{P} > \text{As}$, because it is the softest acid among the three trihalides [3–6].

2. Experimental

All preparations and manipulations were carried out in polyethylene glove bags under a nitrogen atmosphere.

2.1. Chemicals

Arsenic trihalides were prepared as described in a previous paper [7]. *N,N*-diphenylbenzamine (Aldrich Chemical Co. Inc.), triphenylphosphine (BDH Chemicals Ltd.) and triphenylarsine (Aldrich Chemical Co. Inc.) were used as obtained without further purification. Diethylether p.a. (Merck), acetone p.a. (Merck) and ethanolamine (99%, Casa Americana de Artigos para laboratórios Ltda.) were used as obtained for preparing the calorimetric solvents. Other solvents used in the synthesis of adducts were used as obtained for preparing the calorimetric solvents. Other solvents used in the synthesis of adducts were purified by distillation and stored over Linde 4A molecular sieves.

2.2. Analytical

Carbon, hydrogen and nitrogen contents were determined by microanalytical procedures. Halogen analysis was obtained by gravimetry using standard 0.1 N AgNO_3 solution, after the adducts had been dissolved in water [8]. Arsenic content was determined by redox titration of the aqueous solution of adduct samples with standard 0.05 N iodine solution, to the appearance of the blue color of starch used as indicator [9].

2.3. Adduct synthesis

The adducts were prepared by the reaction of arsenic trihalides and the ligands in solution. A typical procedure is given below.

2.3.1. $\text{AsCl}_3 \cdot 2\text{AsPh}_3$

To a solution of 1.1 g of AsPh_3 (3.6 mmol) in 10 ml of petroleum ether, 0.3 ml of AsCl_3 (3.6 mmol) was added slowly and dropwise with stirring. The stirring was maintained for at least 3 h. After filtration, the white crystals formed were washed with three portions of 10 ml of petroleum ether, and dried for several hours in vacuo. The compound obtained was stored in a desiccator over calcium chloride. All the adducts were prepared with a molar ratio donor/acceptor of 1/1. In all cases, petroleum ether was used as a solvent for washing. For the adducts of AsBr_3 and AsI_3 , chloroform–toluene and CS_2 –toluene were used respectively as solvents.

2.4. Infrared spectra

These were obtained with sample mulls in nujol sandwiched between NaCl plates for adducts and free ligands, in the region $4000\text{--}400\text{ cm}^{-1}$ using a Perkin-Elmer 1600 series FTIR spectrophotometer.

2.5. Thermal studies

These were made in an argon atmosphere in a Du Pont 951 TG Analyser, with samples varying in mass from 6 to 11 mg (DSC) and from 11 to 15 mg (TG and DTG), and a heating rate of 10 K min^{-1} in the 298–673 K (DSC) and 298–1214 K (TG and DTG) temperature ranges.

2.6. Calorimetric measurements

All the solution calorimetric determinations were carried out in an LKB 8700-1 precision calorimeter as described before [7, 10]. The solution calorimetric measurements were performed by dissolving samples of 15–70 mg of adduct or trihalide in 100 ml of calorimetric solvent and the ligand in the trihalide solution obtained before, maintaining a molar relation equal to the stoichiometry of the adduct.

2.7. Mass spectra

The mass spectra of the compounds were recorded on an HP 5988A mass spectrometer system.

3. Results and discussion

All the adducts obtained were solids. The yields range from 29 to 58%. The yields, melting points, colors, appearance and analytical data are summarized in Table 1. Solid adducts of AsI_3 with NPh_3 , or of AsBr_3 with NPh_3 or AsPh_3 , were not obtained

3.1. Infrared data

The infrared spectra of the adducts show dislocation of some bands and the appearance of new ones when compared with the spectra of the free ligands. The patterns of the spectra of the adducts are similar to those of the free ligands. For phosphine complexes, the band at 1090 cm^{-1} (X-sensitive q) in the free ligand is moved to higher frequencies and greatly increased in intensity in the complexes. A new band at 723 cm^{-1} (x-sensitive r) appeared after complexation. A strong band at 514 cm^{-1} in the free ligand, assigned as an out-of-plane ring deformation moves 26 cm^{-1} to higher frequencies after complexation. These facts are taken as indicative of coordination of the phosphine through the phosphorous atom [1,2,11].

Table 1
Yields in % on preparation, melting points, appearance and analytical data of the adducts

Compound	Yield	M.P./K	Appearance ^b	C		H		N		Halogen		Arsenic	
				Calcd.	Found	Calcd.	Found	Calcd.	Found	Calcd.	Found	Calcd.	Found
AsCl ₃ NPh ₃	29	613 ^a	gr.pw.	50.7	50.8	3.5	3.4	3.3	3.1	24.9	25.2	17.6	17.2
AsCl ₃ PPh ₃	35	458-60	wh.cr.	67.0	67.0	4.7	4.5	-	-	11.0	10.8	7.7	7.8
AsCl ₃ ·3/2AsPh ₃	50	490-1	s.ye.cr.	50.6	50.8	3.5	3.5	-	-	16.6	16.7	23.4	23.4
AsBr ₃ ·PPh ₃	61	362-4	s.br.pw.	37.5	37.1	2.6	2.5	-	-	41.6	42.2	13.0	13.0
AsI ₃ ·PPh ₃	58	383	or.pw.	30.1	29.7	2.1	2.0	-	-	53.0	52.5	10.4	10.5
AsI ₃ ·2AsPh ₃	12	395-7	or.pw.	40.5	39.9	2.8	2.6	-	-	35.6	35.3	7.0	7.1

^a No melting till 613 K.

^b Key: gr., green; wh., white; ye., yellow; br., brown; or., orange; pw., powder; cr., crystals; s., slightly.

The infrared spectrum of the arsine complexes shows new bands at 743 cm^{-1} (x-sensitive r) and 466 cm^{-1} (x-sensitive y) and the band observed at 1074 cm^{-1} in the free ligand is moved to higher frequencies after complexation, indicating coordination of arsine through the arsenic atom [12,13].

The infrared spectrum of $\text{AsCl}_3 \cdot \text{NPh}_3$ shows a new band at 721 cm^{-1} (x-sensitive r) and the bands observed at 1074 cm^{-1} (x-sensitive y) and 622 cm^{-1} (out-of-plane ring deformation) in the free ligand are moved to higher frequencies after complexation, indicating coordination through the nitrogen atom [11]. Table 2 shows the extracted IR spectral data of the adducts.

3.2. Thermal studies

Thermogravimetry and derivative thermogravimetry of two compounds show a loss of mass in a single step, indicating that the arsenic trihalide and the ligand are lost together. The TG and DTG curves of three compounds show two mass-loss steps: the first with elimination of the trihalide (or part of it) and part of the ligand (or all the ligand); and the second with evolution of the rest of the ligand (or all the ligand) or the rest of the trihalide. Only in the case of $\text{AsCl}_3 \cdot \text{NPh}_3$, do the TG and DTG curves show five steps of mass loss. The melting points of the adducts showed decomposition on melting. They are not stable in the liquid phase. Only in the case of $\text{AsCl}_3 \cdot \text{NP}_3$ is there no apparent melting until 613 K: a black residue is obtained. It is probable that this compound is degraded in five successive steps that leave carbon as a residue [14].

The DSC curves of the adducts are consistent with the TG and DTG data. They present several endothermic peaks. For nearly all the compounds, two endothermic peaks are observed. The first is due to melting of the compound as it is near the capillary melting temperature. It is also near the temperature at which the mass loss begins, indicating that the compounds are unstable in the liquid phase. The second peak is due to a redox process of degradation of the ligands [14]. For the adduct $\text{AsCl}_3 \cdot \text{NPh}_3$, the first endothermic peak observed in the DSC curve is probably due to elimination of

Table 2
Infrared data for ligands and their complexes (cm^{-1})^a

Compound	x-sens.q	x-sens.r	Out-of-plane ring deformation	x-sens.y
NPh_3	1074 m		622 m	
$\text{AsCl}_3 \cdot \text{NPh}_3$	1136 s	721 m	652 m	
PPh_3	1090 m		514 s	
$\text{AsCl}_3 \cdot 3\text{PPh}_3$	1120 m	722 s	541 s	
$\text{AsBr}_3 \cdot \text{PPh}_3$	1120 s	724 s	538 s	
$\text{AsI}_3 \cdot \text{PPh}_3$	1119 s	723 s	540 s	
AsPh_3	1074 m			
$\text{AsCl}_3 \cdot 3/2\text{AsPh}_3$	1184 s	743 m	688 s	466 s
$\text{AsI}_3 \cdot 2\text{AsPh}_3$	1120 m	722 m		436 w

^a Notation used is from Whiffen [11]. Intensity of bands: s, strong; m, medium; w, weak.

AsCl₃, as the temperature of this peak is near the temperature of vaporization of AsCl₃ and the observed enthalpy value is near the enthalpy of vaporization of AsCl₃. The second endothermic peak, observed at 500 K, is due to a redox process of degradation of NPh₃ [14]. The first endothermic peak observed at 342 K for AsCl₃·3PPh₃ is probably due to a crystalline transition as there is no mass loss at this temperature. Table 3 lists the thermoanalytical data of the compounds.

3.3. Mass spectra

The mass spectra of the compounds did not show the parent ion. They resembled the spectra of free ligands plus fragmentation of the adducts [15].

3.4. Calorimetric measurements

The standard enthalpies of dissolution of arsenic trihalide ligands and complexes ($\Delta_f H^\ominus$) were obtained as previously reported [7]. Table 4 gives these standard thermochemical values. Uncertainty intervals given in this table are twice the standard deviations of the means of about five replicate measurements on each compound. Combined errors were calculated from the square root on the sum of the square of the component errors.

From the standard enthalpies of dissolution, the standard enthalpies of the acid/base reactions ($\Delta_r H^\ominus$), the standard enthalpies of formation ($\Delta_f H^\ominus$), the standard enthalpies of decomposition ($\Delta_D H^\ominus$), the lattice standard enthalpies ($\Delta_M H^\ominus$) and the standard enthalpies of the Lewis acid/base reactions in the gaseous phase ($\Delta_r H^\ominus(\text{g})$) can be obtained by using the appropriate thermochemical cycles [7,16].

Table 3
Thermoanalytical data of the compounds AsX₃·nL

Compound	%Mass lost		TG temperature range/K	Species lost	DSC peak temperature/K	Enthalpy/kJ mol ⁻¹
	Calc.	Obs.				
AsCl ₃ ·NPh ₃	100	72.8	311–1214	-AsCl ₃ -NPh ₃	329	46.2
		27.2 ^a			500	23.7
AsCl ₃ ·3PPh ₃	100	99.7	373–650	-AsCl ₃ -3PPh ₃	342	2.2
					402 ^b	63.3
AsCl ₃ ·3/2AsPh ₃	72.0	72.0	418–598	-AsCl ₃ -0.8AsPh ₃	432	49.9
	28.0	27.4	598–918	-0.7 AsPh ₃	572	15.3
AsBr ₃ ·PPh ₃	54.5	56.4	336–508	-AsBr ₃	339	3.4
	45.5	43.2	508–563	-Ph ₃ P	382	19.7
AsI ₃ ·PPh ₃	68.3	71.4	363–513	-0.5AsI ₃ -PPh ₃	348 ^b	24.0
	31.7	27.7	513–544	-0.5AsI ₃		
AsI ₃ ·2AsPh ₃	100	99.7	391–507	-AsI ₃ -2AsPh ₃	390 ^b	53.6

^a Residue.

^b Two overlapping peaks.

Table 4
Enthalpies of dissolution at 298.15 K

Compound	Calorimetric solvent ^a	Number of experiments	$\Delta_i H^\ominus / (\text{kJ mol}^{-1})$
AsCl ₃ (l)	25% dieth.eth.in acet.	4	-13.34 ± 0.21
NPh ₃ (s)	1:1 AsCl ₃ -25% dieth.eth.in acet	5	25.48 ± 0.86
AsCl ₃ ·NPh ₃ (s)	25% dieth.eth.in acet.	5	165.14 ± 2.35
AsCl ₃ (l)	50% dieth.eth.in acet.	4	-38.73 ± 1.75
AsPh ₃ (s)	3/2:1 AsCl ₃ -50% dieth.eth.in acet	5	29.04 ± 0.99
AsCl ₃ 3/2 AsPh ₃ (s)	50% dieth.eth.in acet.	5	52.37 ± 1.14
AsCl ₃ (l)	10% EA in acet.	5	-280.63 ± 1.98
PPh ₃ (s)	3:1 AsCl ₃ -10% EA in acet.	5	57.72 ± 0.78
AsCl ₃ ·3PPh ₃ (s)	10% EA in acet.	5	48.50 ± 1.64
AsBr ₃ (s)	20% c.hex.in acet.	5	-25.66 ± 0.63
PPh ₃ (s)	1:1 AsBr ₃ -20% c.hex. in acet.	5	13.60 ± 0.30
AsBr ₃ ·PPh ₃ (s)	20% c.hex. in acet.	4	6.68 ± 0.10
AsI ₃ (s)	10% EA in acet.	8	-254.44 ± 2.58
PPh ₃ (s)	1:1 AsI ₃ -10% EA in acet.	4	21.02 ± 0.55
AsI ₃ ·PPh ₃ (s)	10% EA in acet.	5	-188.13 ± 3.46
AsPh ₃ (s)	2:1 AsI ₃ -10% EA in acet.	6	43.11 ± 0.60
AsI ₃ ·2AsPh ₃ (s)	10% EA in act.	4	-201.23 ± 1.90

^a 25% or 50% (v/v) diethyl ether in acetone; 10% (v/v) ethanolamine in acetone; 20% (v/v) cycle hexane in acetone.

The $\Delta_i H^\ominus(\text{g})$ values can be used to calculate the standard enthalpy of the As-donor Atom Bonds [16]. Table 5 lists the values obtained for all these thermochemical parameters for the adducts. For the determination of $\Delta_i H^\ominus(\text{g})$, it was necessary to assume that the molar standard enthalpy of sublimation of each adduct was equal to the enthalpy of sublimation of one mole of ligand [7,16,20,21], as melting points, thermal studies and mass spectra showed that the adducts decompose on heating and were not found in the gaseous phase.

Based on the $\Delta_i H^\ominus$ values for a series of adducts of the same stoichiometry and the same ligand, the acidity order $\text{AsBr}_3 < \text{AsI}_3$ is obtained. The same sequence is obtained by using \bar{D} (As-P) values. This means that AsI_3 is a better acid than AsBr_3 for PPh_3 . This is expected because AsI_3 is a softer acid than AsBr_3 . If we compared the \bar{D} (As Donor atom) values for a series of adducts of the same stoichiometry and the same trihalide, taking values from the literature for adducts of arsenic trihalides with other amines [7,14,22], we obtain the basicity sequence $\text{PPh}_3 > \text{An}$ (for AsCl_3) and $\gamma\text{-mpy} > \beta\text{-mpy} \cong \text{dimerin} > \text{PPh}_3 > o\text{-chloron}$ (for 1:1 adducts of AsI_3) and $\text{py} > \text{AsPh}_3$ (for 1:2 adducts of AsI_3). This means the affinity sequence $\text{P} > \text{N}$ for AsCl_3 and $\text{N} > \text{P}$ or $\text{N} > \text{As}$ for AsI_3 . The expected affinity sequence towards soft acceptors is $\text{N} \ll \text{P} > \text{As}$ [3]. The inversion of the expected order is due to the donor properties of the ligand which are highly dependent upon the atomic environment of the donor atom. The type of bonding formed is also important in determining the relative strength of the interaction [23].

Table 5
Summary of the thermochemical results/(kJ mol⁻¹)

Compound	$\Delta_f H^\ominus$	$\Delta_f H^\ominus$	$\Delta_f H^\ominus$ or $\Delta_f H^\ominus$	$\Delta_M H^\ominus$	$\Delta_p H^\ominus$	$\Delta_f H^\ominus(g)$	$\bar{D}(As\text{-don.at.})$
AsCl ₃ (l)	-305.0 ^a						
AsBr ₃ (s)	-197.5 ^a						
AsI ₃ (s)	-58.2 ^a						
NPh ₃ (s)	234.7 ± 3.3 ^b						
PPh ₃ (s)	218.0 ± 10.7 ^c						
AsPh ₃ (s)	309.8 ± 6.7 ^c						
AsCl ₃ ·NPh ₃ (s)	-153.0 ± 2.5			-288.5	245.0 ± 3.5	-196.5	196.5
AsCl ₃ ·PPh ₃ (s)	-271.4 ± 2.7			-603.5	560.0 ± 17.5	-507.3	169.1
AsCl ₃ /2AsPh ₃	-62.1 ± 2.3			-253.0	209.5 ± 12.8	-154.7	103.1
AsBr ₃ ·PPh ₃	-18.7 ± 0.7	1.76		-182.4	114.9 ± 17.3	-86.2	86.2
AsI ₃ ·PPh ₃	-45.3 ± 4.4	114.5		-236.5	141.5 ± 17.8	-140.3	140.3
AsI ₃ ·2AsPh ₃	-10.1 ± 3.3	551.3		-301.7	206.7 ± 13.0	-203.4	101.7

^a Ref. [17]. ^b Ref. [18]. ^c Ref. [19].

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