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Thermochemistry of adducts of bidentate N- and O-ligands with arsenic trihalides

P.O. Dunstan

Instituto de Química, Universidade Estadual de Campinas, C.P. 6154, CEP 13081-970, Campinas, São Paulo, Brazil

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Abstract

The adducts $AsX_3 \cdot nL$ (where L is 2,2′-bipyridine (Bipy) or 2,2′-bipyridine *N,N*′-dioxide ($BipyO_2$), X is Cl, Br or I and n is 1, 1.5 or 2) have been synthesized and characterized by melting points, elemental analysis, thermal studies and infrared spectroscopy. By means of calorimetric measurements in solution, the following thermochemical parameters 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 enthalpies of the Lewis acid/base reactions in the gaseous phase ($\Delta_r H^\ominus(g)$). The mean standard enthalpies of arsenic-nitrogen and arsenic-oxygen bonds have been estimated.

INTRODUCTION

Pyridine and pyridine *N*-oxide ligands are known to form coordination compounds with arsenic trihalides and their preparation, characterization and calorimetric study have been reported recently [1, 2]. The present paper reports the results of a similar study on the compounds of 2,2′-bipyridine (Bipy) and 2,2′-bipyridine *N,N*′-dioxide ($BipyO_2$) with arsenic trihalides. In the cases of pyridine and pyridine *N*-oxide, coordination takes place through the nitrogen atom and through the oxygen atom, respectively. The same is to be expected for Bipy and $BipyO_2$. It could also be expected that the presence of two nitrogen atoms in Bipy and two oxygen atoms in $BipyO_2$ would lead to chelation with the arsenic atom. Complexes of Bipy and $BipyO_2$ with transition element ions have been reported in the literature [3-5]. The same is true for adducts of Bipy with arsenic trihalides [6, 7]. However no thermochemical data for these last compounds are available. No information about the enthalpy of the arsenic-nitrogen bond may be found in the literature. The mean arsenic-donor-atom bond energies in pyridine and pyridine *N*-oxide adducts of arsenic trihalides [1, 2] range from 121 to 168 $kJ\,mol^{-1}$ and from 107 to 116 $kJ\,mol^{-1}$, respectively. In the present paper the mean As-N and As-O bond energies are determined for the adducts of arsenic trihalides with the heterocyclic N and *N*-oxide ligands Bipy and $BipyO_2$.

EXPERIMENTAL

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

Chemicals

Arsenic trihalide was prepared as described in a previous paper [1]. 2,2′-Bipyridine was purified by recrystallization from ethanol according to the method described by Gallagher et al. [8]. 2,2′-Bipyridine *N,N*-dioxide was synthesized as described in the literature [3]. Solvents used in the synthesis of adducts were purified by distillation and stored over Linde 4 Å molecular sieves.

Analytical section

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 [9]. Arsenic content was determined by redox titration of the aqueous solution of adducts samples, with standard 0.05 N iodine solution, to the appearance of the blue color of starch used as an indicator [10].

Adduct synthesis

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

$AsCl_3 \cdot Bipy$

To a solution of 0.50 ml of $AsCl_3$ (6.0 mmol) in 5 ml of ethanol, 0.93 g (6.0 mmol) of bipyridine in 10 ml of ethanol 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 20 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.

Infrared spectra

These were obtained with sample mulls in nujol sandwiched between NaCl plates for adducts and free ligands, on a Perkin Elmer 1600 Series FTIR spectrophotometer.

Thermal studies

These were made in a nitrogen atmosphere in a Du Pont 951 TG Analyser and Du Pont 910 DSC equipment, with samples varying in mass from 3 to 12 mg (TG), and from 0.7 to 3 mg (DSC) and a heating rate of 10 K min^{-1}.

Calorimetric measurements

All the solution calorimetric determinations were carried out in an LKB 8700-1 precision calorimeter as described before [1, 11]. The solution calorimetry measurements were performed dissolving samples of 5–100 mg of adduct or AsX_3 in 90.0 ml of calorimetric solvent and the ligand in the AsX_3 solution, maintaining a molar relation equal to the stoichiometry of adduct.

RESULTS AND DISCUSSION

All the complexes prepared were solids. The yields range from 34% to 79%. The yields, melting points, colors, appearance and analytical data are summarized in Table 1.

Infrared data

The IR spectra of Bipy adducts show dislocation and splitting of some bands, and the appearance of new bands when compared with the spectra of free Bipy. In the region 1520–1462 cm^{-1} two new strong bands appear and another two bands appear at 1322 and 800 cm^{-1}, all of which are absent in the free Bipy and are due to adduct formation [4].

The IR spectra of $BipyO_2$ adducts show shifts in frequencies with respect to free $BipyO_2$ of characteristic bands due to the stretching and bending vibrations of the N–O bond (regions 1300–1200 and 880–830 cm^{-1}, respectively). The observed average shift of the mid-point of the first vibration to lower frequencies after complexation is about 24–26 cm^{-1}. The second vibration is slightly dislocated to lower frequencies after complexation. These facts indicate the decrease of the N–O order after coordination of the $BipyO_2$ [12]. Table 2 shows the IR frequencies observed for $BipyO_2$ and its adducts in these two regions.

TABLE 1

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

Compound	Yield	M.P./K	Appearance [a]	C		H		N		Halogen		Arsenic	
				Calcd.	Found	Calcd.	Found	Calcd.	Found	Calcd.	Found	Calcd.	Found
$AsCl_3 \cdot Bipy$	53	456	wh. cr.	–	–	–	–	8.30	8.45	31.52	31.39	22.20	22.38
$AsBr_3 \cdot Bipy$	62	512	s. pi. pw.	–	–	1.71	1.70	5.95	5.89	50.92	50.50	15.91	15.83
$AsI_3 \cdot Bipy$	79	451	or. pw.	19.63	19.37	1.32	1.34	4.58	4.56	62.23	62.21	–	–
$AsCl_3 \cdot 1.5BipyO_2$	34	468	s. ye. cr.	38.87	39.23	2.61	2.71	9.06	9.28	22.94	22.80	–	–
$AsBr_3 \cdot 2BipyO_2$	34	472	s. ye. pw.	34.76	35.08	2.33	2.46	8.11	8.09	34.69	34.84	–	–
$AsI_3 \cdot 2BipyO_2$	36	405	re. br. pw.	28.87	28.68	1.94	1.96	6.73	6.64	45.76	45.80	–	–

[a] Key: wh., white; pi., pink; or., orange; ye., yellow; br., brown; re., reddish; cr., crystals., pw., powder; s., slightly.

TABLE 2

Observed frequencies (cm^{-1}) of $BipyO_2$ and its adducts [a]

Compound	NO		Compound	NO	
	Stretch	Bend		Stretch	Bend
$BipyO_2$	1262 vs 1255 vs	852 s 840 s	$AsBr_3 \cdot 2BipyO_2$	1256 vs 1210 s	839 s
$AsCl_3 \cdot 1.5BipyO_2$	1259 vs 1211 s	842 s	$AsI_3 \cdot 2BipyO_2$	1265 s 1210 w	842 s

[a] Intensity of bands: vs, very strong; s, strong; w, weak.

Thermal studies

The thermogravimetry of the Bipy complexes shows the loss of ligand and arsenic trihalide together in a single step. The DSC curves consistent with TG data present several endothermic peaks. Only in the case of $AsCl_3 \cdot Bipy$ was an exothermic peak also observed. The capillary melting points of these adducts showed decomposition on melting. They are unstable in the liquid phase. Based on the mass spectra of AsX_3 adducts [13] and of Bipy [14] it may be concluded that they are also unstable in the gaseous phase. The double endothermic peak observed in the DSC curves of $AsCl_3$ and $AsBr_3$ adducts may be due to a crystalline transition followed by melting of the adduct [15]. In the case of the AsI_3 adduct a splitting doublet is observed that may be attributed to crystalline transitions as there is no mass loss at the temperature it is observed. The exothermic peak observed in the $AsCl_3$ adduct may be due to redox degradation of Bipy [14, 15]. The endothermic peak at 518 K observed in the AsI_3 adduct is due to melting of the adduct. Anyway, AsX_3 and Bipy or fragments of Bipy are lost together in the temperature range of the TG data indicated in Table 3. The thermogravimetry of $BipyO_2$ adducts show a three-step mass loss. The DSC curves that are consistent with TG data present several endothermic and exothermic peaks. Only in the case of the $AsCl_3$ adduct were double endothermic peaks also observed. The capillary melting points of the adducts showed decomposition on melting. They are unstable in the liquid phase. Based on the mass spectra of AsX_3 adducts [13] and of $BipyO_2$ [5] it may be concluded that they are also unstable in the gaseous phase. The first double endothermic peak observed in the DSC curve of the $AsCl_3$ adduct may be due to separation and evaporation of part of $AsCl_3$ as the temperature and enthalpy of the peak are near the temperature and enthalpy of vaporization of $AsCl_3$. The second double peak observed may be due to melting followed by redox processes of $BipyO_2$ degradation [5, 15]. The $AsBr_3$ shows one endothermic peak in the DSC curve that is due to melting of the adduct as

TABLE 3

Thermochemical data of the compounds $AsX_3 \cdot nL$

Compound	% Mass lost		Temperature range/K	Species lost [a]	DSC peak temperature/K	Enthalpy/kJ mol^{-1}
	Calc.	Obs.				
$AsCl_3 \cdot$ Bipy	100	98.78	430–645	$-AsCl_3$ – Bipy	437 [b]	362.1
					639	−81.2
$AsBr_3 \cdot$ Bipy	100	99.66	471–521	$-AsBr_3$ – Bipy	488 [b]	361.4
$AsI_3 \cdot$ Bipy	100	98.45	533–583	$-AsI_3$ – Bipy	445	12.8
					455	37.7
					518	50.3
$AsCl_3 \cdot 1.5BipyO_2$	39.10	31.51	387–432	$-AsCl_3$	365 [b]	54.8
	56.69	59.99	432–578	$-O_2 - p$	430 [b]	112.4
	4.21	4.50	578–1123	$-(1/12)C_5H_4N$		
$AsBr_3 \cdot 2BipyO_2$	45.53	46.07	472–489	$-AsBr_3$	473	44.0
	45.99	42.40	489–567	$-O_2 - p$	564	−109.2
	9.04	8.29	567–936	$-(1/15)C_5H_4N$	596	−25.8
					673	−277.7
$AsI_3 \cdot 2BipyO_2$	62.44	60.86	418–473	$-AsI_3-O_2$	406	16.8
					412	−15.4
					429	95.9
	13.44	12.02	473–493	−p		
	24.12	25.73	493–673	$-(18/7)C_5H_4N$	512	8.7

[a] p, Decomposition products of $BipyO_2$ are HCN, C_2H_2, H_2. [b] Double peak.

TABLE 4

Enthalpies of dissolution at 298.15 K

Compound	Calorimetric solvent [a]	Number of experiments	i	$\Delta_i H^\ominus$/kJ mol^{-1}
$AsCl_3(l)$	25%EA-EtOH	5	1	-387.28 ± 3.28
Bipy(s)	1:1 $AsCl_3$-25%EA-EtOH	5	2	48.53 ± 1.26
$AsCl_3 \cdot$ Bipy(s)	25%EA-EtOH	5	3	-124.08 ± 0.79
$AsBr_3(s)$	25%EA-EtOH	5	1	-286.51 ± 2.41
Bipy(s)	1:1 $AsBr_3$-25%EA-EtOH	5	2	42.08 ± 1.54
$AsBr_3 \cdot$ Bipy(s)	25%EA-EtOH	5	3	-164.76 ± 0.03
$AsI_3(s)$	10%EA-EtOH	5	1	-212.30 ± 2.56
Bipy(s)	1:1 AsI_3-10%EA-EtOH	5	2	16.08 ± 0.62
$AsI_3 \cdot$ Bipy(s)	10%EA-EtOH	5	3	-180.04 ± 0.10
$AsCl_3(l)$	30%EA-H_2O	5	1	-472.02 ± 3.79
$BipyO_2(s)$	1:1.5 $AsCl_3$-30%EA-H_2O	5	2	24.39 ± 1.06
$AsCl_3 \cdot 1.5BipyO_2(s)$	30%EA-H_2O	5	3	-155.42 ± 1.86
$AsBr_3(s)$	30%EA-H_2O	5	1	-233.00 ± 1.10
$BipyO_2(s)$	2:1 $AsBr_3$-30%EA-H_2O	5	2	29.50 ± 1.25
$AsBr_3 \cdot 2BipyO_2(s)$	30%EA-H_2O	5	3	-102.98 ± 0.69
$BipyO_2(s)$	2:1AsI_3-10%EA-EtOH	5	2	45.24 ± 1.93
$AsI_3 \cdot 2BipyO_2$	10%EA-EtOH	5	3	-153.57 ± 0.72

[a] 10% or 25% (v/v) ethanolic enthanolamine, 30% (v/v) aqueous ethanolamine.

the peak temperature is equal to the melting point observed. Several exothermic peaks are then observed. They may be due to the degradation of $BipyO_2$ [5, 15]. The DSC curves of AsI_3 adduct show an endothermic peak at 406 K that is due to the melting of the adduct as it occurs at the temperature of melting observed for the adduct. Following this peak there is an exothermic peak that may be due to the degradation of $BipyO_2$ [2, 15]. A third endothermic peak is then observed that is due to the melting of AsI_3 as it has the temperature and enthalpy equal to those of AsI_3. Finally, another endothermic peak is observed that may be due to the decomposition of the degradation products of $BipyO_2$ [5, 15]. The first step of mass loss in the TG data of the adducts may be attributed to the elimination of trihalide or part of it. The AsI_3 adduct also eliminates degradation products of $BipyO_2$. The second and third steps may be due to elimination of the degradation products of $BipyO_2$. Table 3 lists the thermoanalytical data of the adducts.

Calorimetric measurements

The standard integral enthalpies of dissolution of arsenic trihalides, ligands and adducts ($\Delta_i H^\ominus$) were obtained as previously reported [1]. Table 4 gives these standard thermochemical values. From the standard enthalpies

TABLE 5

Summary of the thermochemical results (in kJ mol^{-1})

Compound	$\Delta_{\mathrm{r}}H^{\ominus}$	$\Delta_{\mathrm{f}}H^{\ominus}$	$\Delta_{\mathrm{s,l}}^{\mathrm{g}}H^{\ominus}$	$\Delta_{\mathrm{M}}H^{\ominus}$	$\Delta_{\mathrm{D}}H^{\ominus}$	$\Delta_{\mathrm{r}}H^{\ominus}(\mathrm{g})$	$\bar{D}$(As–N) or $\bar{D}$(As–O)
$AsCl_3(l)$		−305.0 [a]	43.5 [a]				
$AsBr_3(s)$		−197.5 [a]	67.5 [a]				
$AsI_3(s)$		−58.2 [a]	95.0 [a]				
Bipy(s)		216.4 ± 7.4 [b]	81.93 ± 0.33 [c]				
$BipyO_2(s)$		16.6 ± 5.2 [d]	180 ± 10 [d]				
$AsCl_3 \cdot Bipy(s)$	−214.67 ± 3.60	−303.3		−340.1	296.60 ± 3.62	−258.2	129.1
$AsBr_3 \cdot Bipy(s)$	−79.67 ± 2.86	−60.8		−229.1	161.60 ± 2.88	−147.2	73.6
$AsI_3 \cdot Bipy(s)$	−16.18 ± 2.64	142.0		−193.1	98.11 ± 2.66	−111.2	55.6
$AsCl_3 \cdot 1.5BipyO_2(s)$	−292.21 ± 4.35	−572.3		−606	562 ± 11	−426	142
$AsBr_3 \cdot 2BipyO_2(s)$	−100.52 ± 1.80	−264.8		−528	461 ± 11	−349	87
$AsI_3 \cdot 2BipyO_2(s)$	−13.49 ± 3.29	−38.5		−469	374 ± 11	−289	72

[a] Ref. 16, [b] Ref. 17, [c] Ref. 18, [d] Ref. 5.

of dissolution, the standard enthalpies of formation of the adducts ($\Delta_f H^\ominus$), the standard enthalpies of decomposition of the adducts ($\Delta_D H^\ominus$), the lattice standard enthalpies of the adducts ($\Delta_M H^\ominus$) and the standard enthalpies of the Lewis acid/base reactions in the gaseous phase ($\Delta_r H^\ominus(g)$) can be determined [1]. The $\Delta_r H^\ominus(g)$ values can be used to calculate the standard enthalpy of the arsenic–nitrogen or arsenic–oxygen bond ($\bar{D}$(As–N) or $\bar{D}$(As–O)), being equal to $-\Delta_r H^\ominus(g)/n$. Table 5 lists the values for all these parameters.

The melting points, TG and DSC studies of the adducts show that these compounds decompose on heating and are not stable in the liquid phase and probably not in the gaseous phase. For the determination of $\Delta_r H^\ominus(g)$, the molar standard enthalpy of sublimation of each adduct ($\Delta_s^g H^\ominus$) was taken as the enthalpy of sublimation of one mole of ligand. Measurements on some adducts that sublime and correlations of $\Delta_s^g H^\ominus$(adduct) calculated for several forms confirm this assumption [13, 19].

Based on the $\Delta_r H^\ominus$ values for the series of Bipy adducts, the acidity order $AsCl_3 > AsBr_3 > AsI_3$ is obtained. Based on $\bar{D}$(As–N) values, the same sequence for acidity is obtained. Assuming equivalence of the donor atoms for Bipy, it is possible to compare $\bar{D}$(As–N) for pyridine (py) and Bipy adducts of arsenic trihalides. Thus, $\bar{D}$(As–N) is higher for py than for Bipy adducts, showing that py is a better ligand than Bipy for arsenic trihalides (e.g. $\bar{D}$(As–N) values in the $AsCl_3$ adducts are 154 and 129 kJ mol^{-1} for py and Bipy respectively).

Based on the $\Delta_r H^\ominus$ and $\bar{D}$(As–O) values for the series of $BipyO_2$ adducts of the same stoichiometry, the acidity order $AsBr_3 > AsI_3$ is obtained. Assuming equivalence of the donor atoms for $BipyO_2$ it is possible to compare $\bar{D}$(As–O) of pyridine *N*-oxide (pyNO) and $BipyO_2$ adducts of arsenic trihalides. Thus $\bar{D}$(As–O) is higher for pyNO than for $BipyO_2$ in the cases of $AsBr_3$ and AsI_3 adducts. The contrary is true for the $AsCl_3$ adducts (e.g. $\bar{D}$(As–O) values are respectively 107 and 87 kJ mol^{-1} for pyNO and $BipyO_2$ adducts of $AsBr_3$). This means that pyNO is a better ligand than $BipyO_2$ for $AsBr_3$ and AsI_3, whereas $BipyO_2$ is a better ligand than pyNO for $AsCl_3$.

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REFERENCES

1 P.O. Dunstan and C. Airoldi, J. Chem. Eng. Data, 33 (1988) 93.
2 P.O. Dunstan, Thermochim. Acta, 181 (1991) 143.
3 P.G. Simpson, A. Vinciguerra and J.V. Quagliano, Inorg. Chem., 2 (1963) 282.
4 S.P. Sinha, Spectrochim. Acta, 20 (1964) 879.

5 M.L.C.P. da Silva, A.P. Chagas and C. Airoldi, J. Chem. Soc. Dalton Trans., (1988) 2113.
6 W.R. Roper and C.J. Wilkins, Inorg. Chem., 3 (1964) 500.
7 M.J. Deveney and M. Webster, J. Chem. Soc. A, (1970) 1643.
8 M.J. Gallagher, D.P. Graddon and A.R. Sheikh, Thermochim. Acta, 27 (1978) 269.
9 I.M. Kolthoff and E.B. Sandall, Tratado de Química Analítica Cuantitativa, Libreria y Editorial Nigar S.R.L., Buenos Aires, 3rd edn., 1956, p. 371.
10 Ref. 9, p. 19.
11 P.O. Dunstan, Thermochim. Acta, 197 (1992) 201.
12 S. Kida, J.V. Quagliano, J.A. Walmsley and S.Y. Tyree, Spectrochim. Acta, 19 (1963) 189.
13 P.O. Dunstan and L.C.R. dos Santos, Thermochim. Acta, 156 (1989) 163.
14 N.G. Keats and L.A. Summers, J. Heterocycl. Chem., 13 (1976) 369.
15 S. Gordon, J. Chem. Educ., 40 (1963) A87.
16 D.D. Wagman, W.H. Evans, V.B. Parker, R.H. Schumm, I. Halow, S.M. Bailey, K.L. Churney and R.I. Nuttall, J. Phys. Chem. Ref. Data, 11 (1982) 2.
17 C. Airoldi, M.L.C.P. Silva and A.P. Chagas, J. Chem. Soc. Dalton Trans., (1986) 1913.
18 M. Faour and T.S. Akasheh, J. Chem. Soc. Perkin Trans. 2, (1985) 811.
19 A.P. Chagas and C. Airoldi, Polyhedron, 8 (1989) 1093.