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THERMOCHEMISTRY OF PYRIDINE- AND PICOLINE-*N*-OXIDE COMPLEXES OF ARSENIC TRIHALIDES

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ABSTRACT

The complexes $AsX_3 \cdot nL$ (where L = pyridine-*N*-oxide (pyNO), α, β, or γ-picoline-*N*-oxide (α, β-, or γ-piCONO), $n = 1$ or 2 for X = Cl, $n = 1$, 3/2 or 2 for X = Br and $n = 1$, 3/2 or 2 for X = I) were prepared and characterised by melting point, elemental analysis, thermogravimetric studies and infrared spectroscopy. From the enthalpies of dissolution in ethanol or 50% 2.4 N HCl in ethanol of the complexes, arsenic trihalides and ligands at 298.15 K, the standard enthalpies ($\Delta_r H^\ominus$) for the Lewis acid/base reactions were determined. From the $\Delta_r H^\ominus$ values, the standard enthalpies of formation of arsenic trihalides and the standard enthalpies of formation of the ligands, the standard enthalpies of formation of the complexes ($\Delta_f H^\ominus$) were calculated. The standard enthalpies of decomposition of the complexes ($\Delta_D H^\ominus$), as well as the lattice standard enthalpies ($\Delta_M H^\ominus$) and the standard enthalpies of the Lewis acid/base reactions in the gaseous phase ($\Delta_r H^\ominus(g)$), were calculated by means of thermochemical cycles, and the mean standard enthalpies of the arsenic–oxygen bonds ($\bar{D}$ (As–O)) were estimated.

The mean energies of the As–O bonds range from 98 to 125 kJ mol^{-1} in these complexes. The thermochemical data suggested the order $AsCl_3 > AsBr_3 > AsI_3$ for acidity and γ-piCONO > pyNO > α-piCONO for basicity. Correlation between several of the thermochemical parameters, and between the thermochemical parameters of these complexes and parameters of the complexes of non-oxidized ligands, were established.

INTRODUCTION

In a recent article [1], we described the synthesis, characterisation and thermochemistry of complexes of arsenic trihalides with pyridine, and β- and γ-picoline, for which mean arsenic–nitrogen coordinate bond energies were determined. This paper describes the interaction of arsenic trihalides with pyridine-*N*-oxide, and α-, β- and γ-picoline-*N*-oxide, forming complexes in which the oxygen atom is the coordinating atom of the ligands. The strength of the As–O bond in amide complexes of arsenic trihalides ranges from 89 to 150 kJ mol^{-1} [2]. In the present paper, we report the calorimetric measurements made on a series of trihalide complexes, which are analogous with the complexes of pyridine and picoline, in order to study the influence of introducing an oxygen atom into the ligand structure and to compare the strengths of the As–N and As–O coordinate bonds.

EXPERIMENTAL

Due to the moisture sensitivity and toxic nature of the compounds involved, all preparations were carried out in polyethylene glove bags under a dry nitrogen atmosphere.

Chemicals

The arsenic trihalides were prepared as described before [1]. The ligands were prepared by methods outlined in the literature [3–5]. Solvents were purified by distillation.

Analytical

Carbon, hydrogen and nitrogen were determined by microanalytical procedures. Halogen analysis was by gravimetry using N/10 $AgNO_3$ solution [6], following dissolution of the complexes in water. Arsenic content was determined by redox titration of the aqueous solutions of the complexes with standard 0.05 M iodine solution, until the starch indicator turned blue [7].

Synthesis of the complexes

The complexes were prepared as described in previous papers [1,2]. A typical procedure is given here for $AsCl_3 \cdot pyNO$. A solution of 2.27 g of pyNO (23.8 mmol) in 20 ml of benzene was added slowly, dropwise with stirring to a solution of 2.0 ml of $AsCl_3$ (23.8 mmol) in 20 ml of benzene. The stirring was maintained for at least three hours. After removal of the solvent, the white solid formed was washed with three 20 ml portions of petroleum ether, and then dried for several hours in a vacuum. The compound obtained was stored in a desiccator over calcium chloride.

For the synthesis of the $AsBr_3$ complexes, chloroform, carbon tetrachloride or 50% CCl_4–*n*-hexane were used as solvents, and for the AsI_3 complexes, CS_2 was used.

Infrared spectra

The spectra were obtained with complex and free ligand sample mulls in Nujol sandwiched between NaCl plates, using a Perkin–Elmer 180 spectrophotometer.

Thermogravimetric studies

These were carried out in a nitrogen atmosphere in a Du Pont 1090 thermogravimetric analyser, with samples varying in weight from 2.41 to 9.41 mg 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 previously described [1,2].

RESULTS AND DISCUSSION

Nearly all the arsenic trihalide complexes were prepared with a molar ratio of 1 : 1 between AsX_3 and the ligands. In the preparation of $AsBr_3 \cdot 2$pyNO and $AsI_3 \cdot 2\gamma$-piCONO, a molar ratio of 1 : 2 was used because products of indefinite stoichiometries, were obtained with a 1 : 1 molar ratio. The yields of the complexes obtained ranged from 60 to 100%. The melting points, colours and analytical data of the complexes are summarised in Table 1.

Infrared data

The infrared spectra of pyNO complexes showed a small dislocation, splitting or decrease in intensity of some bands when compared with the spectrum of free pyNO. Coordinated pyNO is distinguished from free pyNO by a decrease in the frequency of the NO stretching vibration (at 1250 cm^{-1} in the free ligand) upon coordination [8]. The AsI_3 complex showed the smallest decrease. The main infrared bands and their assignments [8–10] for pyNO and its complexes are presented in Table 2.

The infrared spectra of α-piCONO complexes showed a decrease in the frequency of the NO stretching vibration (at 1252 cm^{-1} in the free ligand) upon coordination. There were also small dislocations of some of the other bands. The spectra of the mono- and bis-complexes of $AsBr_3$ are similar; only small differences were observed. The NO stretching vibration was split into two bands and a new strong band appeared at 762 cm^{-1} in the bis-complex. Table 3 shows the main infrared bands and their assigments [11] for α-piCONO and its complexes.

The infrared spectra of β-piCONO complexes are similar to that of the free ligand, except for small dislocations and a decrease in intensity of some bands when compared with the spectrum of free α-piCONO. Appreciable dislocations toward lower frequencies are observed after coordination for the absorption attributed to NO stretching vibration in the free ligand

TABLE 1

Melting points, appearance, yield and analytical data of the complexes

Compound	mp[a] (°C)	Appearance[b]	Yield (%)	% C		% H		% N		% As		% Halogen	
				Calc.	Found	Calc.	Found	Calc.	Found	Calc.	Found	Calc.	Found
$AsCl_3 \cdot$pyNO	71	wh cr	65	21.73	20.80	1.82	2.00	5.07	4.95	27.11	27.22	38.48	38.25
$AsCl_3 \cdot \alpha$-piCONO	98	wh cr	64	24.82	24.75	2.43	2.62	4.82	4.65	25.80	26.02	36.62	36.56
$AsCl_3 \cdot 2\beta$-piCONO	120	wh cr	67	36.08	36.20	3.53	3.90	7.01	6.90	18.75	19.01	26.62	26.85
$AsCl_3 \cdot \gamma$-piCONO	70	wh cr	51	24.82	24.98	2.43	2.61	4.82	4.85	25.80	25.49	36.62	36.68
$AsBr_3 \cdot 2$pyNO	99	s ye pw	50	23.79	24.00	2.00	2.26	5.55	5.70	14.84	14.72	47.48	47.27
$AsBr_3 \cdot \alpha$-piCONO	65	s ye pw	60	17.01	16.46	1.66	1.97	3.31	3.58	17.68	17.74	56.57	56.36
$AsBr_3 \cdot 2\alpha$-piCONO	60	s ye pw	68	27.05	26.70	2.65	3.00	5.26	5.07	14.06	14.36	44.98	44.79
$AsBr_3 \cdot \beta$-piCONO	67	s ye pw	78	17.01	16.80	1.66	1.70	3.31	2.99	17.68	17.55	56.57	56.40
$2AsBr_3 \cdot 3\gamma$-piCONO	79	s ye pw	88	22.60	21.70	2.21	2.30	4.39	4.34	15.66	15.57	50.12	50.17
$AsI_3 \cdot 2$pyNO	99	or pw	51	18.60	18.50	1.56	1.70	4.34	4.00	11.60	11.68	58.95	58.68
$AsI_3 \cdot \alpha$-piCONO	71	or pw	100	12.76	13.03	1.25	1.47	2.48	2.36	13.70	13.61	67.41	67.24
$2AsI_3 \cdot 3\beta$-piCONO	71	br pw	57	17.45	17.20	1.14	1.40	3.39	3.40	12.10	12.21	61.47	61.62
$AsI_3 \cdot 2\gamma$-piCONO	93	or pw	60	21.39	21.19	2.09	2.19	4.16	4.13	11.12	11.39	56.49	56.90

[a] Uncorrected.

[b] Key: wh, white; ye, yellow; or, orange; br, brown; s, slightly; pw, powder; cr, crystal.

TABLE 2

Assignment of infrared frequencies (cm^{-1}) of pyNO and its complexes [a]

pyNO	$AsCl_3 \cdot pyNO$	$AsBr_3 \cdot 2pyNO$	$AsI_3 \cdot 2pyNO$	Assignment
3065m,sh	3084m	3056m,sh	3065s,sh	CH str. (ν)
	3064m			
	3044m			
1598s	1615m	1613w	1619w	Ring def. in-plane (α)
	1591m	1566m		
1551s	1535m	n.o.	n.o.	
	1517m			
1498m	1507m	1508w	n.o.	
	1443m			
	1328m	1313w	n.o.	CH in-plane def. (β)
	1255m			
1250s,b	1198s	1180s	1244m	NO str. (ν)
1168s	1183s		1150w	CH in-plane def. (β)
	1148w	1143m		
	1096w	1090m		
1073m	1068w	1058m		
	1048w			
1010s	1023m	1020m	1018w	Ring breathing
926w	953w	940s	938w	CH out-of-plane def. (γ)
		850s		
840s	820s	832s	834w	NO def. (δ)
		810s	800m	
760s	769s	760s	765m	CH out-of-plane def. (γ)
			740m	
			720m	
670s	665s	680m	665s	? Ring def. out-of-plane (ϕ)
		660s		

[a] Intensity of bands: vs, very strong; s, strong, m, medium; w, weak; sh, shoulder; b, broad; n.o., not observed.

(double band at 1280–1270 cm^{-1}). Table 4 shows the infrared data and their assigments [12] for β-piCONO and its complexes.

The γ-piCONO complexes showed infrared spectra similar to that of free γ-piCONO. The NO stretching vibration of the free ligand (1246 cm^{-1}) suffered dislocation toward lower frequencies upon coordination. A small dislocation and a decrease of some other bands were also observed. The main infrared bands and their assigments [13] for γ-piCONO and its complexes are shown in Table 5.

Thermogravimetric data

Thermogravimetry of the compounds indicated three different decomposition schemes: in the first, ligand and arsenic trihalide are lost together in a unique step; in the second, evolution of arsenic trihalide and part of the

TABLE 3

Assignment of infrared frequencies (cm^{-1}) of α-piCONO and its complexes [a]

α-piCONO	$AsCl_3 \cdot \alpha$-piCONO	$AsBr_3 \cdot \alpha$-piCONO	$AsBr_3 \cdot 2\alpha$-piCONO	$AsI_3 \cdot \alpha$-piCONO	Assignment
3030m	n.o.	3017m	3040m	3040m	CH str. (ν)
1612m	1620m	1621s	1618s	1618s	CC and CN str. (ν)
1555w	1574w	1566w	1576m	1571w	CC and CN str. (ν)
1491s	1490m	1487m	1486m	1483s	CC and CN str. (ν)
1252s	1189s	1190s	1190s 1178s	1210m	NO str. (ν)
1146w	1151w	1156m	1156w	1157m	CH in-plane def. (β)
1109m	1111m	1113m	1113s	1109m	CH in-plane def. (β)
1049m	1031m	1031m	1032m	1032m	CH in-plane def. (β)
850s	837s	837s	838s	803s	CH out-of-plane def. (γ)
755s	768s	780vs	780vs	762m	
			762vs	690m	

[a] See Table 2 for key.

ligand (or ligand and part of the AsI$_3$) occurs in the first step followed by the loss of the rest of the ligand (or the rest of the AsI$_3$) in the second step; in the third scheme, the loss of mass occurs in three steps: the first with elimination of part of the arsenic trihalide, the second with elimination of

TABLE 4

Assignment of infrared frequencies (cm^{-1}) of β-piCONO and its complexes [a]

β-piCONO	$AsCl_3 \cdot 2\beta$-piCONO	$AsBr_3 \cdot \beta$-piCONO	$2AsI_3 \cdot 3\beta$-piCONO	Assignment
3047m	3029m	3055m	n.o.	CH str. (ν)
1602m	1612m	1618m	n.o.	CC and CN str. (ν)
1562w	1575w	n.o.	n.o.	CC and CN str. (ν)
1483m	1486m	1494sh	n.o.	CC and CN str. (ν)
1420m	1423m	n.o.	n.o.	CC and CN str. (ν)
1280s	1248s	1215w	1260w	NO str. (ν)
1270s				
1167sh	1172s	1160w	1164w	?
1160s	1170m	1150m	1145w	CH in-plane str. (β)
1015s	1025m	1015m	1028w	Ring breathing
948m	931s	933w	922w	CH out-of-plane str. (γ)
907w	910w			CH out-of-plane str. (ν)
793s	813s	808w	797m	
748s	774s		778m	
676s	742m	720m	718m	
665s	670s	664s	664s	

[a] See Table 2 for key.

TABLE 5

Assignment of infrared frequencies (cm^{-1}) of γ-piCONO and its complexes [a]

γ-piCONO	$AsCl_3$· γ-piCONO	$2AsBr_3$· 3γ-piCONO	AsI_3· 2γ-piCONO	Assignment
3080m	3030m	3050sh	3020m	CH str. (ν)
1626w	1629s	1627m	1629m	CC and CN str. (ν)
1487s	1488s	1484m	1491m	CC and CN str. (ν)
1246s	1206s	1202m	1207w	NO str. (ν)
1180s	1189s	1188m	1176w	CH in-plane str. (β)
1122w	1127w	n.o.	1114m	CH in-plane str. (β)
1041s	1041s	1038s	1034m	CH in-plane str. (β)
854s	862sh	850w	854w	? NO def. (δ)
830s	833vs	830m	831sh	CH out-of-plane str. (γ)
	782vs	792w	824s	
			800s	
750vs	740s	757m	752m	

[a] See Table 2 for key.

the rest of the arsenic trihalide and part of the ligand, and the third with elimination of the rest of the ligand. The thermoanalytical data of the complexes is shown in Table 6.

Calorimetric measurements

The standard enthalpies of dissolution of arsenic trihalide, ligands and complexes ($\Delta_i H^\ominus$) were obtained as previously reported [1,2]. Table 7 gives these standard thermochemical values. From the standard enthalpies of dissolution, the standard enthalpies of acid/base reactions ($\Delta_r H^\ominus$) were determined. Using appropriate thermochemical cycles and applying Hess's Law, we obtained the standard enthalpies of decomposition ($\Delta_D H^\ominus$), the standard lattice enthalpies ($\Delta_M H^\ominus$) and the standard enthalpies of acid/base reactions in the gaseous phase ($\Delta_r H^\ominus(g)$). From the $\Delta_r H^\ominus(g)$ values, the mean standard enthalpy of the arsenic–oxygen bond ($\bar{D}$(As–O)) was calculated [1,2]. The values of these parameters are listed in Table 8. The melting points and the thermogravimetric studies of the complexes showed that they decompose on heating. For the determination of $\Delta_r H^\ominus(g)$, it was assumed that the molar standard enthalpy of sublimation of each complex ($\Delta_s^g H^\ominus$) was equal to the enthalpy of sublimation of one mole of ligand [2]. For the calculation of the standard enthalpies of formation of the complexes, it was necessary to calculate the enthalpies of sublimation of the ligands, α-, β- and γ-piCONO, which are not available in the literature, using a group contribution method [17–19], adding the difference between the enthalpy of vaporisation of α-, β- or γ-picoline and pyridine [20] to the enthalpy of sublimation of pyNO.

TABLE 6

Thermoanalytical data of the compounds $AsX_3\cdot n$L

Compound	Weight loss (%)		Temperature range (K)	Attribution	mp (K)
	Calcd.	Obs.			
$AsCl_3\cdot$pyNO	77.1	77.0	318–478	$-AsCl_3$, $-1/3$pyNO	344
	22.9	19.0	478–713	$-2/3$pyNO	
	0	5.0	713–1223		
$AsCl_3\cdot\alpha$-piCONO	87.5	84.0	318–478	$-AsCl_3$, $-2/3\alpha$-piCONO	371
	12.5	13.0	478–653	$-1/3\alpha$-piCONO	
	0	3.0	653–1223		
$AsCl_3\cdot 2\beta$-piCONO	50.8	50.0	368–463	$-AsCl_3$, -1.5β-piCONO	393
	49.2	47.0	463–578	$-9/5\beta$-piCONO	
	0	3.0	578–1223		
$AsCl_3\cdot\gamma$-piCONO	74.9	74.0	368–483	$-AsCl_3$, $-1/3\gamma$-piCONO	343
	25.1	23.0	483–913	$-2/3\gamma$-piCONO	
	0	3.0	913–1223		
$AsBr_3\cdot 2$pyNO	65.6	68.0	343–518	$-3/4AsBr_3$, -1pyNO	372
	15.6	14.0	518–583	$-1/4AsBr_3$	
	18.0	15.0	583–873	-1pyNO	
	0	3.0	873–1223		
$AsBr_3\cdot\alpha$-piCONO	100	100	353–798	$-AsBr_3$, $-\alpha$-piCONO	338
	0	0	798–1000		
$AsBr_3\cdot 2\alpha$-piCONO	79.5	85.0	318–503	$-AsBr_3$, $-\alpha$-piCONO	333
	20.5	15.0	503–803	$-\alpha$-piCONO	
	0	0	803–1223		
$AsBr_3\cdot\beta$-piCONO	66.8	68.0	373–508	$-9/10AsBr_3$	340
	13.9	11.0	508–513	$-1/10$ $AsBr_3$, $-1/4\beta$-piCONO	
	19.3	20.0	513–943	$-3/4\beta$-piCONO	
	0	1.0	943–1223		
$2AsBr_3\cdot 3\gamma$-piCONO	54.8	56.0	313–478	$-5/3AsBr_3$	352
	45.2	42.0	478–1118	$-1/3AsBr_3$, -3γ-piCONO	
	0	2.0	1118–1223		
$AsI_3\cdot 2$pyNO	85.9	88.0	343–488	-2pyNO, $-4/5AsI_3$	372
	14.1	9.0	488–613	$-1/5AsI_3$	
	0	3.0	613–1223		
$AsI_3\cdot\alpha$-piCONO	83.8	82.0	383–473	$-\alpha$-piCONO, $-4/5AsI_3$	344
	16.2	14.0	473–568	$-1/5AsI_3$	
	0	4.0	568–1223		
$2AsI_3\cdot 3\beta$-piCONO	85.3	87.0	402–483	-3β-piCONO, $-8/5AsI_3$	344
	14.7	11.0	483–528	$-2/5AsI_3$	
	0	2.0	528–1223		
$AsI_3\cdot 2\gamma$-piCONO	83.8	82.0	368–498	-2γ-piCONO, $-4/5AsI_3$	366
	16.2	14.0	498–568	$-1/5AsI_3$	
	0	4.0	568–1223		

TABLE 7

Enthalpies [a] of dissolution at 298.15 K

Compound	Calorimetric solvent	$\Delta_i H^\ominus$ (kJ mol^{-1})
$AsCl_3$(l)	EtOH	($i=1$) -111.82 ± 0.12
pyNO(s)	1 : 1 $AsCl_3$–EtOH	($i=2$) 11.56 ± 0.42
$AsCl_3\cdot$pyNO(s)	EtOH	($i=3$) -35.46 ± 0.42
$AsCl_3$(l)	EtOH	($i=1$) -119.14 ± 0.49
α-piCONO(s)	1 : 1 $AsCl_3$–EtOH	($i=2$) 16.96 ± 0.31
$AsCl_3\cdot\alpha$-piCONO	EtOH	($i=3$) -47.63 ± 0.05
$AsCl_3$(l)	2.4 N HCl–EtOH	($i=1$) -62.56 ± 0.69
β-piCONO(s)	2 : 1 $AsCl_3$–2.4 N HCl–EtOH	($i=2$) -16.82 ± 0.28
$AsCl_3\cdot2\beta$-piCONO(s)	2.4 N HCl–EtOH	($i=3$) 40.37 ± 0.43
$AsCl_3$(l)	EtOH	($i=1$) -115.72 ± 0.60
γ-piCONO(s)	1.1 $AsCl_3$–2.4 N HCl–EtOH	($i=2$) 12.08 ± 0.37
$AsCl_3\cdot\gamma$-piCONO(s)	EtOH	($i=3$) -12.79 ± 0.34
$AsBr_3$(s)	2.4 N HCl–EtOH	($i=1$) -34.33 ± 0.55
pyNO(s)	2.1 $AsBr_3$–2.4 N HCl–EtOH	($i=2$) 5.54 ± 0.10
$AsBr_3\cdot$2pyNO	2.4 N HCl–EtOH	($i=3$) 36.04 ± 0.62
$AsBr_3$(s)	2.4 N HCl–EtOH	($i=1$) -34.64 ± 0.52
α-piCONO(s)	1.1 $AsBr_3$–2.4 N HCl–EtOH	($i=2$) -2.22 ± 0.17
$AsBr_3\cdot\alpha$-piCONO(s)	2.4 N HCl–EtOH	($i=3$) 8.94 ± 0.07
$AsBr_3$(s)	2.4 N HCl–EtOH	($i=1$) -31.58 ± 0.01
α-piCONO(s)	1.2 $AsBr_3$–2.4 N HCl–EtOH	($i=2$) -12.28 ± 0.71
$AsBr_3\cdot2\alpha$-piCONO(s)	2.4 N HCl–EtOH	($i=3$) 24.12 ± 0.22
$AsBr_3$(s)	2.4 N HCl–EtOH	($i=1$) -34.64 ± 0.52
β-piCONO(s)	1.1 $AsBr_3$–2.4 N HCl–EtOH	($i=2$) -9.18 ± 0.36
$AsBr_3\cdot\beta$-piCONO(s)	2.4 N HCl–EtOH	($i=3$) 20.82 ± 0.11
$AsBr_3$(s)	2.4 N HCl–EtOH	($i=1$) -32.16 ± 0.47
γ-piCONO(s)	3 : 2 $AsBr_3$–2.4 N HCl–EtOH	($i=2$) 3.24 ± 0.21
$2AsBr_3\cdot3\gamma$-piCONO(s)	2.4 N HCl–EtOH	($i=3$) 18.67 ± 0.85
AsI_3(s)	2.4 N HCl–EtOH	($i=1$) 14.97 ± 0.17
pyNO(s)	2 : 1 AsI_3–2.4 N HCl–EtOH	($i=2$) -12.91 ± 0.74
$AsI_3\cdot$2pyNO(s)	2.4 N HCl–EtOH	($i=3$) 58.55 ± 0.92
AsI_3(s)	2.4 N HCl–EtOH	($i=1$) 14.97 ± 0.17
α-piCONO	1 : 1 AsI_3–2.4 N HCl–EtOH	($i=2$) -3.17 ± 0.09
$AsI_3\cdot\alpha$-piCONO	2.4 N HCl–EtOH	($i=3$) 42.23 ± 0.46
AsI_3(s)	2.4 N HCl–EtOH	($i=1$) 11.96 ± 0.70
β-piCONO(s)	3 : 2 AsI_3–2.4 N HCl–EtOH	($i=2$) -11.14 ± 0.11
$2AsI_3\cdot3\beta$-piCONO	2.4 N HCl–EtOH	($i=3$) 47.19 ± 0.12
AsI_3(s)	2.4 N HCl–EtOH	($i=1$) 14.97 ± 0.17
γpiCONO(s)	2 : 1 AsI_3–2.4 N HCl–EtOH	($i=2$) 36.99 ± 0.54
$AsI_3\cdot2\gamma$-piCONO	2.4 N HCl–EtOH	($i=3$) 97.83 ± 0.83

[a] Five experiments were performed in all cases.

Considering the $\Delta_r H^\ominus$ values for complexes of the same stoichiometry with a fixed ligand, we obtained the acidity order: $AsCl_3 > AsBr_3 > AsI_3$. The basicity order, γ-piCONO > pyNO > α-piCONO, was obtained if $AsCl_3$

TABLE 8

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

Compound	$\Delta_r H^\ominus$	$\Delta_f H^\ominus$	$\Delta_s^g H^\ominus$	$\Delta_M H^\ominus$	$\Delta_D H^\ominus$	$\Delta_r H^\ominus$(g)	$\bar{D}$(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]				
pyNO(s)		7.7 ± 0.8 [b]	81.9 ± 1.5 [b]				
α-piCONO(s)		10.3 ± 0.8 [c]	84.2 ± 2.3 [d]				
β-piCONO(s)		8.8 ± 0.7 [c]	86.2 ± 2.2 [d]				
γ-piCONO(s)		12.9 ± 0.9 [c]	87.0 ± 2.1 [d]				
$AsCl_3$·pyNO(s)	−64.80 ± 0.61	−362.1		−190.2	146.7 ± 1.6	−108.3	108.3
$AsCl_3$·α-piCONO(s)	−54.55 ± 0.58	−349.3		−182.3	138.8 ± 2.4	−98.1	98.1
$AsCl_3$·2β-piCONO(s)	−119.75 ± 0.86	−407.2		−335.7	292.2 ± 2.4	−249.5	124.8
$AsCl_3$·γ-piCONO(s)	−90.80 ± 0.78	−383.0		−221.4	177.9 ± 2.2	−134.4	134.4
$AsBr_3$·2pyNO(s)	−64.83 ± 0.83	−246.4		−291.6	228.6 ± 1.7	−214.2	107.2
$AsBr_3$·α-piCONO(s)	−45.80 ± 0.55	−232.5		−197.5	130.3 ± 2.4	−113.3	113.3
$AsBr_3$·2α-piCONO(s)	−67.98 ± 0.74	−244.4		−303.9	236.4 ± 2.4	−219.7	109.9
$AsBr_3$·β-piCONO(s)	−64.64 ± 0.64	−252.8		−218.3	150.8 ± 2.3	−132.1	132.1
$2AsBr_3$·3γ-piCONO(s)	−47.59 ± 0.99	−225.2		−245.6	178.1 ± 2.3	−158.9	105.9
AsI_3·2pyNO(s)	−56.49 ± 1.19	−99.3		−315.3	220.3 ± 1.9	−233.4	116.7
AsI_3·α-piCONO(s)	−30.30 ± 0.50	−78.3		−209.6	114.6 ± 2.4	−125.4	125.4
$2AsI_3$·3β-piCONO(s)	−46.37 ± 0.72	91.4		−270.7	175.7 ± 2.3	−184.5	123.0
AsI_3·2γ-piCONO(s)	−45.87 ± 1.00	−78.3		−314.9	219.9 ± 2.3	−227.9	114.0

[a] Ref. 14.
[b] Ref. 15.
[c] Ref. 16.
[d] See text.

was used as the common acceptor. However, this basicity order seems to invert when $AsBr_3$ or AsI_3 are used as the common acceptor. The data indicate that γ-piCONO is the best base for $AsCl_3$ but that pyNO is the best base for AsI_3 and α-piCONO is the best base for mono-complexes of $AsBr_3$. The acidity order obtained is that expected on the basis of an inductive effect. The expected order for basicity on the basis of an inductive effect is γ-piCONO > β-piCONO ≈ α-piCONO > pyNO [1].

Considering the $\bar{D}$(As–O) values obtained, the same basicity order is observed although the acidity order is inverted. This means than in the gaseous phase, AsI_3 is the best acid for α-piCONO and $AsCl_3$ is the worst. The parameters $\Delta_f H^{\ominus}$ (complexes), $\Delta_M H^{\ominus}$ and $\Delta_D H^{\ominus}$ also showed this behaviour.

Comparing the mean energy of the As–O bonds obtained for these complexes with the mean energy of the As–N bonds obtained for pyridine and picoline complexes of arsenic trihalides [1] of the same stoichiometry, it is observed that the introduction of an oxygen atom in the ligand structure tends to weaken the arsenic–ligand interaction. The As–N bond is always stronger than the corresponding As–O bond. It would be expected, on the basis of an inductive effect, that the oxygen atom should form a stronger bond to the arsenic atom than the nitrogen atom. Also, in terms of the hard/soft acid/base (HSAB) [21–23] concept, because of the slighty harder oxygen atom, the As–O bond should be stronger than the As–N bond for $AsCl_3$ complexes and weaker for AsI_3 complexes. Clearly, the nature of the bond formed between the donor and acceptor atoms is important in determining the relative strength of the interaction [1,2–4].

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