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Thermochemistry of liquid adducts of amides formed from AsX_3 (X=Cl, Br)

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Abstract

Liquid adducts of the general formula AsX_3L (X=Cl, Br; L=*N*,*N*-dimethylformamide (DMF), *N*,*N*-dimethylacetamide (DMA), tetramethylurea (TMU)] were synthesized and characterized by elemental analysis, IR spectroscopy and mass spectra. From enthalpies of dissolution $(\Delta_i H^0_\mathrm{m})$ in 1,2-dichloroethane at 298.15 K and the appropriate thermochemical cycle, standard molar enthalpies have been determined for Lewis acid–base reaction $(\Delta_\mathrm{r} H^0_\mathrm{m})$, formation $(\Delta_\mathrm{f} H^0_\mathrm{m})$, decomposition $(\Delta_\mathrm{D} H^0_\mathrm{m}$ or $\Delta_\mathrm{M} H^0_\mathrm{m})$, Lewis acid–base reaction in gas phase $(\Delta_\mathrm{f} H^0_\mathrm{m})$ and the mean arsenic–oxygen bond enthalpies, $\langle D \rangle$ (As–O). These thermochemical parameters give the acidity $AsCl_3>AsBr_3$ and basicity TMU>DMA>DMF. © 1998 Elsevier Science B.V.

Keywords: Arsenic; *N*,*N*-Dimethylacetamide; *N*,*N*-Dimethylformamide; Tetramethylurea; Thermochemistry

1. Introduction

Amides have been the subject of many investigations for the understanding of biological processes associated with living organisms because amides are useful models for peptide and protein studies [1,2]. Amides bond to acceptors via the oxygen [3–5] donor atom. However, in rare cases, nitrogen also acts as a Lewis base centre to coordinate metal atoms [1,6,7]. Some thermochemical studies of amide–accepter interactions have been used to determine certain energy parameters. From the standard molar enthalpies of formation of adducts in the gas phase, the corresponding mean enthalpies of dissociation of element–ligand bonds were calculated. These data are an important clue for understanding the nature of the element–ligand bonds in adducts as well as in chelates [8–11].

The aim of this publication is to report on the synthesis, characterization, and calorimetric measurements on adducts of tetramethylurea (TMU), dimethylacetamide (DMA) and dimethylformamide (DMF) with arsenic tribromide and trichloride. The data were collected for the purpose of obtaining the enthalpy changes for the formation of these adducts and to establish the acid–base correlations.

2. Experimental

2.1. Chemicals

The solvents, such as $AsCl_3$, TMU, DMA and DMF, used in all preparations were reagent grade (Carlo Erba). These were purified and dried in vacuum

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[12–14]. The calorimetric solvent, and 1,2-dichloroethane (DCE), chosen for its ability to dissolve the salts, ligands and adducts, was carefully dried and distilled prior to use. All substances used in the calorimetric determinations were rigorously dried in vacuum before preparing the ampoules.

2.2. Preparation

Arsenic tribromide was prepared as previously reported [15]. The adducts were synthesised by reacting the arsenic trihalides and the individual ligands in solution in acetone ($AsCl_3$) or 1,2-dichloroethane ($AsBr_3$) in a 1 : 1 molar ratio of donor : acceptor. The solutes were added dropwise with stirring under anhydrous conditions, and the resulting solution was maintained under stirring for at least 8 h. After filtration and drying under vacuum a viscous liquid was obtained and stored in a desiccator over calcium chloride. The yield of these preparations varied from 59 to 68%. Carbon, hydrogen and nitrogen contents were determined by microanalytical procedures. Halogen assays were carried out gravimetrically by the addition of 0.10 mol dm^{-3} silver nitrate solution to the adducts dissolved in water [16].

2.3. Calorimetric measurements

An LKB 8700-1 isoperibolic precision calorimeter was used for all reaction measurements. Details of the operational procedure, calculation method and accuracy of the instrument have been previously described [8,11,15,17]. The air-sensitive compounds were handled in dried nitrogen to prepare the glass ampoules, containing 20–55 mg of substrate, which were broken into a glass vessel charged with 0.10 dm^3 of calorimetric solvent at 298.15+0.02 K. For each determination, the uncertainty interval is quoted as twice the standard deviation of the mean for at least six measurements. Combined errors were calculated as the square root of the sum of the squares of the component errors.

2.4. Other measurements

Infrared spectra in the 4000–400 cm^{-1} range were obtained with a BOMEM model MB-102 spectrophotometer on sample mulls in Nujol, sandwiched between sodium chloride plates for adducts and free ligands. Mass spectra of the ligands and adducts were recorded on a Hewlett–Packard model 5988A spectrometer with an ionisation energy of 70 eV at 523 K.

3. Results

The results of elemental analyses of the liquid adducts are in complete agreement with the general formula, AsX_3L (X=Cl, Br and L=DMF, DMA, TMU), as observed in Table 1.

The infrared spectra of the adducts show that some bands are shifted when compared with the spectra of the free ligands, however, the main characteristics of the bands in the adducts are similar to those of the free ligands. As expected, the carbonyl stretching frequencies for the three ligands, 1668 (DMF), 1645 (DMA) and 1640 cm^{-1} (TMU) [8], after co-ordination are shifted to 1632, 1612 and 1562 cm^{-1}, respectively, for $AsCl_3$ adducts and to 1635, 1594 and 1555 cm^{-1} for $AsBr_3$ adducts. An opposite behaviour was observed for carbon–nitrogen stretching frequencies at 1450 (DMF), 1500 (DMA), and 1496 cm^{-1} (TMU) [8] in the free ligands, which were shifted to 1465, 1510 and 1542 cm^{-1} in $AcCl_3$ adducts and to 1463, 1512 and 1540 cm^{-1} for $AsBr_3$ adducts. The opposite shifts observed for the CO and CN stretching frequencies are in agreement with the formation of arsenic–oxygen bonds in these adducts [8,11,18].

The mass spectra of the complexes did not show the parent ion and resembled the spectra of the free ligands [8] plus the pure trihalides with the fragments $[AsX_3]^+$, $[AsX_2]^+$, $[AsX]^+$, $[X_2]^+$, $[X]^+$ and $[As]^+$ where (X=Cl or Br).

The standard molar enthalpies of dissolution $(\Delta_i H_m^0)$ of halides AsX_3, ligands L and adducts AsX_3L were obtained as previously reported [8,19,21]. Table 2 lists

Table 1
Mass percentage analysis (obtained values in parentheses) in %

Compound	C	H	N	Halogen
$ASCL_3DMF(l)$	14.2(14.6)	2.8(2.6)	5.5(5.3)	41.9(41.6)
$ASCL_3DMA(l)$	17.9(17.9)	3.4(3.3)	5.2(5.1)	39.7(39.4)
$ASCL_3TMU(l)$	20.2(20.0)	4.0(3.9)	9.4(9.2)	35.8(35.5)
$ASBR_3DMF(l)$	9.3(9.2)	1.8(1.6)	3.6(3.5)	61.9(60.5)
$ASBR_3DMA(l)$	11.9(11.8)	2.2(2.1)	3.6(3.4)	59.7(59.4)
$ASBR_3TUM(l)$	13.9(13.8)	2.8(2.7)	6.5(6.4)	55.7(55.6)

Table 2
Enthalpies of dissolution in 1,2-dichloroethane (DCE) at 298.15 K in kJ mol^{-1}

	Reagent	Solvent	Solution	No. of expts	$\Delta_i H^0_m$
1	DMF(l)	DCE	A_1	7	1.48±0.02
2	AsBr$_3$(l)	A_1	A	6	−22.31±0.08
3	ASBR$_3$DMF (l)	DCE	A_3	7	7.21±0.01
1	DMA(l)	DCE	B_1	7	1.78±0.01
2	AsBr$_3$(l)	B_1	B_2	7	−25.07±0.11
3	ASBR$_3$DMA(l)	DCE	B_3	7	13.03±0.04
1	TMU(l)	DCE	C_1	7	1.85±0.02
2	AsBr$_3$(l)	C_1	C_2	6	−26.52±0.12
3	AsBr$_3$TMU(l)	DCE	C_3	7	18.32±0.06
1	DMF(l)	DCE	D_1	7	1.48±0.02
2	AsCl$_3$(c)	D_1	D_2	7	−20.08±0.11
3	ASCL$_3$DMF(l)	DCE	D_3	7	20.38±0.05
1	DMA(l)	DCE	E_1	7	1.78±0.01
2	AsCl$_3$(c)	E_1	E_2	7	−22.05±0.09
3	ASCL$_3$DMA(l)	DCE	E_3	7	21.99±0.03
1	TMU(l)	DCE	F_1	7	1.85±0.02
2	AsCl$_3$(c)	F_1	F_2	6	−23.00±0.09
3	ASCL$_3$TMU(l)	DCE	F_3	7	22.41±0.04

Table 3
Summary of the thermochemical results in kJ mol^{-1}

Compound	$\Delta_r H^0_m$	$\Delta_f H^0_m$	$\Delta^g_{cr} H^0_m$ or $\Delta^g_l H^0_m$	$\Delta_D H^0_m$	$\Delta_M H^0_m$
DMF(1)		−239.37±1.21 [a]	45.19±0.63 [d]		
DMA(l)		−278.32±1.51 [a]	50.10±0.20 [e]		
TMU(l)		−254.39 [b]	51.12 [f]		
AsCl$_3$(l)		−305.0 [c]	43.50 [c]		
AsBr$_3$(cr)		−197.50 [c]	67.50 [c]		
AsCl$_3$DMF(l)	−38.98±0.12	−475.85		84.2	151.7
AsCl$_3$DMA(l)	−42.26±0.12	−518.08		92.4	159.9
AsCl$_3$TMU(l)	−43.56±0.10	−495.45		94.7	162.2
AsBr$_3$DMF(l)	−28.04±0.08	−572.41		73.2	116.7
AsBr$_3$DMA(l)	−36.32±0.11	−619.64		86.4	129.6
AsBr$_3$TMU(l)	−42.99±0.15	−602.38		94.1	136.6

[a] See Ref. [25].
[b] See Ref. [26].
[c] See Ref. [27].
[d] See Ref. [14].
[e] See Ref. [28].
[f] See Ref. [29].

the values. By applying Hess's law, the standard molar enthalpies ($\Delta_r H^0_m$) of the acid–base reactions, AsX_3(cr,l)+L(l)=AsX_3L(l) were calculated. From the standard molar acid–base reactions listed in Table 3, the standard molar enthalpies of formation ($\Delta_f H^0_m$) of the adducts in the liquid phase were obtained by means of the expression: $\Delta_f H^0_m(\text{adduct}) = \Delta_r H^0_m + \Delta_f H^0_m(\text{ligand}) + \Delta_f H^0_m(\text{halide})$. The enthalpies of formation of the ligands and halides, as given in literature, are shown in Table 3.

From $\Delta_r H^0_m$ values, the standard molar enthalpies for the reactions

$$AsX_3L(l) = AsX_3(l, cr) + L(g); \quad \Delta_D H^0_m$$

$$AsX_3L(l) = AsX_3(g) + L(g); \quad \Delta_M H^0_m$$

can be obtained by means of thermodynamic cycles. These values provide information about the facility of ligand release during heating and the energetics of formation of liquid adducts from gaseous reagents. From appropriate cycles

$$\Delta_D H_m^0 = -\Delta_r H_m^0 + \Delta_l^g H_m^0(L)$$

and

$$\Delta_M H_m^0 = \Delta_D H_m^0 + \Delta_{l,cr}^{1} H_m^0(AX_3)$$

The last terms in both expressions are the enthalpies of vaporisation of the ligand L and liquid halide or sublimation of the solid halide. From values tabulated in the literature, as shown in Table 3, the desired enthalpy changes were calculated and are listed in Table 3.

The standard molar enthalpies of the Lewis acid–base reactions in the gaseous phase $(\Delta_r H_m^0, g)$ can be determined by using the appropriate thermochemical cycles [19–21], and the mean arsenic–oxygen bond enthalpies can be estimated [8,11,22]. The values obtained are listed in Table 3. For the determination of the standard enthalpy of the Lewis acid–base reactions in the gaseous phase, the molar enthalpy of sublimation of each adduct was assumed equal to the enthalpy of vaporisation of one mole of ligand [11,20,22,23]. This assumption is based on the observations from thermal studies and mass spectra that the adducts decompose on heating and were not found in the gaseous phase.

The mean arsenic–oxygen bond enthalpy was calculated based on the expression $\langle D\rangle(\text{As–O}) = \Delta_r H_m^0, g$ because, in all cases, the arsenic is coordinated to the ligand through the oxygen atom to form a monoadduct. As indicated in Table 3, these values show the sequence TMU>DMA>DMF, for both halides. Furthermore, $\langle D\rangle$(As–O) for arsenic chlorides are greater than those for the corresponding bromides. For example, for AsX_3DMF, $\langle D\rangle$(As–O) is 71.5 and 106.5 kJ mol^{-1} for bromide and chloride, respectively.

4. Discussion

The standard molar enthalpies of formation of the adducts in the condensed phase are related to the donor strengths of the ligands [10]. The present system is a favourable one to demonstrate this because the adducts have identical stoichiometry in the liquid phase, which is rare; $\Delta_r H_m^0$ values listed in Table 3 show that the interaction effect is clearly larger for chlorides, indicating an acidity order $AsCl_3$>$AsBr_3$. This sequence agrees with the complete series $AsCl_3$> $AsBr_3$>AsI_3 obtained with other ligands [8–11]. In addition, within the Group VA series of elements an acidity order $BiCl_3$>$SbCl_3$ was established for adducts with 1 : 1 and 1 : 2 stoichiometries [8]. ^{13}C-NMR studies involving $SbCl_3$DMA confirmed a strong antimony–oxygen bond interaction with a decrease of the rational barrier in the bonded ligand [24].

The great ability of the tmu ligand to form adducts has also been demonstrated with urea derivatives such as dimethyl- (DMU) and methylureas (MU), to give TMU>DMU>MU. The methyl inductive effect on the basic oxygen centre in TMU forces a more effective interaction with the acidic centre which is reflected in larger bond enthalpes. The sequence of standard molar enthalpy values $(\Delta_r H_m^0)$ obtained from the amide and arsenic halide interactions examined in this study displayed the same trend in basicity of the ligands. But other adducts must be studied to confirm this.

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