Thermochimica Acta, 206 (1992) 13–18
Elsevier Science Publishers B.V., Amsterdam

Thermochemical study of adducts of tetramethylthiourea with antimony and bismuth triiodides

Luiz C.R. dos Santos [a], Severino F. de Oliveira [a], José G.P. Espínola [a] and Claudio Airoldi [b]

[a] *Departamento de Química, CCEN, Universidade Federal da Paraíba, 58040 João Possoa, Paraíba (Brazil)*
[b] *Instituto de Química, Universidade Estadual de Campinas, Caixa Postal 6154, 13081 Campinas, São Paulo (Brazil)*

(Received 29 November 1991)

Abstract

The adducts $MI_3 \cdot tmtu$ (M = Sb, Bi; tmtu = tetramethylthiourea) were prepared, characterized and studied through reaction–solution calorimetry at 298.15 K. The molar standard enthalpy $\Delta_r H_m^\ominus$ of the reaction $MI_3(cr) + tmtu(cr) = MI_3 \cdot tmtu(cr)$ gave -19.84 ± 0.46 and -13.01 ± 0.17 kJ mol^{-1} for Sb and Bi, respectively. From $\Delta_r H_m^\ominus$ values the standard molar enthalpies of formation of the crystalline Sb and Bi adducts were calculated as -158.5 and -201.3 kJ mol^{-1}, respectively. The mean element–sulphur bond enthalpies were also calculated as 122 and 147 kJ mol^{-1} for Sb–S and Bi–S bonds, respectively. The acidity order $AsI_3 > SbI_3 > BiI_3$ was established.

INTRODUCTION

The determination of the thermochemical properties of amides and thioamides is of great importance for the understanding of many biological processes associated with living organisms, because the mentioned compounds are useful models for peptide and protein studies [1]. Investigations related to these kinds of bases in coordination chemistry have emphasized the structural features [2]. Nonetheless, thermochemical studies involving adducts formed with these ligands have enabled the determination of some energetic parameters such as the standard molar enthalpies of formation and the energies of dissociation of element–ligand bonds. These data are important for evaluating the nature of the participation of the ligand in forming element–ligand bonds in complexes [3].

Correspondence to: C. Airoldi, Instituto de Química, Universidade Estadual de Campinas, Caixa Postal 6154, 13081 Campinas, São Paulo, Brazil.

Thermochemical studies related to phosphorus group elements, which have not been extensive, include adducts [4–7] as well as chelates. In this latter class of compounds, the element–sulphur bond enthalpies decrease monotonically from phosphorus to bismuth [8–10], a behaviour which is also followed for zinc family elements [11]. With these latter elements, adducts of the series with thiourea [12,13], thioacetamide [14] and thiobenzamide [14] showed a slight trend of decreasing metal–sulphur bond enthalpies from zinc to mercury.

The synthesis, characterization and thermochemistry of the adducts formed by tetramethylthiourea (tmtu) with antimony and bismuth triiodides will be reported here. Combined with results for arsenic with similar compounds [6], the findings give a general idea about the variation of thermochemical data in the adducts of these elemental series.

EXPERIMENTAL

Reagents

Solvents used in all preparations and for calorimetry were distilled and kept dried. A mixture of methanol with hydrochloric acid was shown to be very suitable in dissolving iodide, the ligand and the adducts in calorimetric determinations.

Preparation methods

Antimony triiodide [15] and bismuth triiodide [16] were prepared by following the methods described. Tetramethylthiourea was added slowly to a stirred solution of SbI_3 in an equimolar mixture of 1,2-dichloroethane and carbon disulphide under anhydrous conditions. A solid started to separate, and reaction was complete after stirring for 1 h. The brown solid $SbI_3 \cdot$ tmtu was filtered off, washed with petroleum ether and dried in vacuo. Analogously, the adduct $BiI_3 \cdot$ tmtu was prepared in an equimolar mixture of 1,2-dichloroethane and ethanol. The iodide content in the adducts was determined gravimetrically by using 0.1 mol dm^3 silver solution [17]. Carbon and hydrogen were determined using a Perkin-Elmer microelemental analyser. Nitrogen content was obtained by the kjeldahl method.

Instruments

Infrared spectra were recorded using Nujol mulls on a Perkin-Elmer 180 spectrophotometer. Thermogravimetric curves were obtained in a dynamic atmosphere of nitrogen using a Du Pont model 1090 thermobalance, with samples varying in weight from 2 to 3 mg and a heating rate of 0.16 K s^{-1}.

TABLE 1

Melting temperatures (K), mass percentage analyses (calculated values in parentheses) and C–N and C–S stretching wavenumbers ($\mathrm{cm^{-1}}$)

Compound	Melting temp. (K)	C	H	N	I	ν(C–N)	ν(C–S)
tmtu						1502	1124
$\mathrm{SbI_3 \cdot tmtu}$	418–422	9.20 (9.50)	1.84 (1.92)	4.38 (4.41)	59.24 (59.89)	1570	1100
$\mathrm{BiI_3 \cdot tmtu}$	423–427	8.02 (8.31)	1.55 (1.66)	3.77 (3.87)	52.00 (52.77)	1576	1110

A Hewlett-Packard 5988 A spectrometer was used for obtaining ligand and adduct mass spectra with 70 eV ionization energy. The reaction–solution calorimetric measurements were performed in an LKB 8700-1 isoperibolic precision calorimetric system [14]. Ampoules containing 5–50 mg of substrate were prepared in a dry-box and broken into the glass reaction vessel charged with 0.10 $\mathrm{dm^3}$ of calorimetric solvent at 298.15 ± 0.02 K.

RESULTS AND DISCUSSION

Elemental analyses of the brown adducts are in complete agreement with the general formula $\mathrm{MI_3 \cdot tmtu}$ (M=Sb, Bi) as observed in Table 1. The infrared spectra of these compounds showed a decrease of the carbon–sulphur stretching frequency from 1124 $\mathrm{cm^{-1}}$ in the free ligand to 1100 and 1110 $\mathrm{cm^{-1}}$ in the antimony and bismuth adducts, respectively. The opposite behaviour was observed with the carbon–nitrogen stretching frequency: from 1502 $\mathrm{cm^{-1}}$ in the free ligand to 1570 and 1576 $\mathrm{cm^{-1}}$ for the same sequence. These shifts indicate metal–sulphur bond formation in these adducts [4,18–20].

The decomposition of the adducts above the melting temperatures was monitored by thermogravimetry. For the antimony compound, a complete weight loss was observed in only one step in the range 428–708 K. This same behaviour was detected for the corresponding arsenic compound [6]. The adduct of bismuth did not show steps which could be attributed to ligand or to iodide, but the mass decreased continuously in the range 476–970 K without leaving a residue.

The mass spectra of the adducts did not show the parent ion. The general profiles of the fragments derived from the ligand [21] are the same for both adducts, i.e. $\mathrm{[(CH_3)_2NCSN(CH_3)_2]^{\cdot+}}$, $\mathrm{[(CH_3)_2NCSH]^{\cdot+}}$, $\mathrm{[(CH_3)_2NCS]^{\cdot+}}$, $\mathrm{[CH_3CSNH]^{\cdot+}}$, or $\mathrm{[CH_3CSCH_3]^{\cdot+}}$, $\mathrm{[CH_3CSN]^{\cdot+}}$, $\mathrm{[(C_2H_5)_2N]^{\cdot+}}$, $\mathrm{[(CH_3)_2NH]^{\cdot+}}$, $\mathrm{[CS]^{\cdot+}}$ or $\mathrm{[C_2H_5NH]^{\cdot+}}$, $\mathrm{[(CH_3)_2N]^{\cdot+}}$ and $\mathrm{[C_2H_4N]^{\cdot+}}$. These peaks are supplemented by the iodide fragments $\mathrm{[MI_3]^{\cdot+}}$, $\mathrm{[MI_2]^{\cdot+}}$, $\mathrm{[MI]^{\cdot+}}$, $\mathrm{[I_2]^{\cdot+}}$, $\mathrm{[I]^{\cdot+}}$ and by $\mathrm{[M]^{\cdot+}}$.

The standard molar enthalpies of formation of the crystalline adducts $\mathrm{MI_3 \cdot tmtu}$ (M = Sb, Bi) were based on the reaction

$$\mathrm{MI_3(cr) + tmtu(cr) = MI_3 \cdot tmtu(cr)} \qquad \Delta_r H_m^\ominus \qquad (1)$$

TABLE 2

Molar enthalpies of dissolution (kJ mol^{-1}) in a mixture of methanol (MeOH)/hydrochloric acid (HCl) solution at 298.15 K

i	Reactant	Solvent	Solution	No. of expts	$\Delta_i H_m^\ominus$
1	SbI_3(cr)	S_1	A_1	4	16.98 ± 0.09
2	tmtu(cr)	A_1	A_2	5	24.23 ± 0.09
3	$SbI_3 \cdot$tmtu(cr)	S_1	A_3	4	61.05 ± 0.20
4	BiI_3(cr)	S_2	B_1	5	20.15 ± 0.02
5	tmtu(cr)	B_1	B_2	4	26.05 ± 0.10
6	$BiI_3 \cdot$tmtu(cr)	S_2	B_2	5	59.21 ± 0.55

The calorimetric solvent used was MeOH+HCl (aq. 1.8 mol dm^{-3}) [S_1] and MeOH+HCl (aq. 2.4 mol dm^{-3}) [S_2].

The standard molar enthalpy was obtained from the reaction–solution enthalpies $\Delta_i H_m^\ominus$ of each reactant and product dissolved sequentially in the calorimetric solvent [14]. Then, $\Delta_r H_m^\ominus = \Delta_1 H_m^\ominus + \Delta_2 H_m^\ominus - \Delta_3 H_m^\ominus$. These results are listed in Table 2. The $\Delta_r H_m^\ominus$ values are useful for comparing the acidity of the metals [22] and calculating the standard molar enthalpies of formation of the adducts by considering also the standard molar enthalpies of formation of metal triiodides [23,24] and the ligand [25]: results are shown in Table 3. The standard molar enthalpies related to the decomposition process of the reactions

$$MI_3 \cdot \mathrm{tmtu(cr)} \Rightarrow MI_3\mathrm{(cr)} + \mathrm{tmtu(g)} \qquad \Delta_D H_m^\ominus \tag{2}$$

$$MI_3 \cdot \mathrm{tmtu(cr)} \Rightarrow MI_3\mathrm{(g)} + \mathrm{tmtu(g)} \qquad \Delta_M H_m^\ominus \tag{3}$$

can be given by the expressions $\Delta_D H_m^\ominus = -\Delta_r H_m^\ominus + n\Delta_{\mathrm{or}}^{\mathrm{g}} H_m^\ominus(\mathrm{tmtu})$ and $\Delta_M H_m^\ominus = \Delta_D H_m^\ominus(MI_3) + \Delta_{\mathrm{cr}}^{\mathrm{g}} H_m^\ominus$. From the enthalpies of sublimation of tmtu [25], and antimony and bismuth triiodides [26] listed in Table 3, both thermochemical quantities were calculated and are presented in Table 3.

To determine the metal–sulphur bond enthalpy of the adducts, information about these compounds in the gaseous phase is desirable [3]. Thus, the enthalpy $\Delta_g H_m^\ominus$ obtained from reaction (4), which is related to $\Delta_M H_m^\ominus$ by

TABLE 3

Auxiliary data and thermochemical results (kJ mol^{-1})

Compound	$\Delta_r H_m^\ominus$	$\Delta_f H_m^\ominus$	$\Delta_{\mathrm{cr}}^{\mathrm{g}} H_m^\ominus$	$\Delta_D H_m^\ominus$	$\Delta_M H_m^\ominus$	$\Delta_g H_m^\ominus$	⟨D⟩ (M–S)
SbI_3(cr)		-100.4	101.7				
BiI_3(cr)		-150	134.3				
tmtu(cr)		-38.3 ± 2.3	83.26 ± 0.2				
$SbI_3 \cdot$tmtu(cr)	-19.84 ± 0.46	-158.5		103.1	204.8	121.5	122
$BiI_3 \cdot$tmtu(cr)	-13.01 ± 0.17	-201.3		96.3	230.6	147.3	147

the expression $\Delta_g H_m^{\ominus} = \Delta_M H_m^{\ominus} - \Delta_s H_m$, where the last value is the enthalpy of sublimation

$$MI_3 \cdot tmtu(g) = MI_3(g) + tmtu(g) \qquad (4)$$

of the adduct. For these adducts, the mean metal–sulphur bond enthalpy ⟨D⟩(M–S) is given by $\Delta_g H_m^{\ominus}$ because the ligand is monodentate. However, this thermochemical value depends on the enthalpy of sublimation of the adduct, which is shown to be unstable during the heating process.

Based on the assumption that $\Delta_s H_m^{\ominus} = \Delta_{cr}^{g} H_m^{\ominus}$(tmtu) (a hypothesis supported by some sublimable adducts [3]) with results that show its validity to within ±10 kJ mol^{-1}, then $\Delta_g H_m^{\ominus}$ was calculated and, consequently, the value of ⟨D⟩(M–S) is also listed in Table 3.

The measured molar standard enthalpy of reaction in the condensed phase for the adduct $AsI_3 \cdot tmtu$ was -34.55 ± 0.38 kJ mol^{-1} [6]. This value is the highest for the sequence of elements. Therefore, from these values the acidity order $AsI_3 > SbI_3 > BiI_3$ can be easily established. This trend in variation is in the opposite direction of that for $\Delta_f H_m^{\ominus}$. On the other hand, for adducts formed among trichlorides and some oxo-monodentate ligands, the acidity order is $BiCl_3 > SbCl_3$ [4].

The mean element–sulphur bond enthalpy for the corresponding arsenic compound was previously determined as 130 kJ mol^{-1}, and the series $AsX_3 \cdot tmtu$ (X=Cl, Br, I) showed an increase in the sequence, i.e., 91, 104 and 130 kJ mol^{-1}, respectively [6]. So, ⟨D⟩ values are in the order Bi > As > Sb within this group of elements. In comparing ⟨D⟩(E–S) and ⟨D⟩(E–O) magnitudes, the following factors must be considered: (i) adducts of pyridine *N*-oxide (pyO), $AsCl_3 \cdot pyO$, gave 108 kJ mol^{-1} for ⟨D⟩(As–O) [7], (ii) for $SbCl_3 \cdot L$ (L = *N,N*-dimethylformamide, *N,N*-dimethylacetamide or tetramethylurea), ⟨D⟩(Sb–O) values vary from 96 to 113 kJ mol^{-1}, and (iii) a somewhat higher range, 113-125 kJ mol^{-1} was determined for $BiCl_3 \cdot 2L$ adducts [4]. The ⟨D⟩(E–O) values suggest an increase from arsenic to bismuth. In spite of the non-existence of equivalent stoichiometric adducts for bismuth and the different halides considered, these values suggest that ⟨D⟩(E–S) is larger than ⟨D⟩(E–O).

The decrease of ⟨D⟩(E–S) values within phosphorus group elements in both the series diethyl- and di-*n*-butyldithiocarbamate chelates, from 180 to 130 and from 206 to 148 kJ mol^{-1}, respectively, was interpreted as a favourable overlap of *d* orbitals of the former element (E) and an increase in hardness properties associated with the latter element (S). Consequently, the harder bismuth should form an unfavourable overlap in bonding with soft sulphur [8–10]. However, the highest ⟨D⟩(Bi–S) value found in tmtu adducts can be related to the change in softness of this element in the presence of iodine, and the increase in size favours conditions that eliminate possible steric hindrance around the coordination site. Support for these arguments can be supplied by other thermochemical determinations.

ACKNOWLEDGEMENT

The authors thanks CNPq for financial support.

REFERENCES

1 S.H. Laurie, in G. Wilkinson (Ed.), Comprehensive Coordination Chemistry, Vol. 2, Pergamon, Oxford, 1987, p. 739.
2 A.G. Onrubia, P. Souza and J.R. Masaguer, Transition Met. Chem., 13 (1988) 384.
3 A.P. Chagas and C. Airoldi, Polyhedron, 9 (1989) 1093.
4 C. Airoldi, Inorg. Chem., 20 (1981) 998.
5 P.O. Dunstan and C. Airoldi, J. Chem. Eng. Data, 33 (1988) 93.
6 P.O. Dunstan and L.C.R. Santos, Thermochim Acta, 156 (1989) 163.
7 P.O. Dunstan, Thermochim. Acta, 181 (1991) 143.
8 C. Airoldi and A.G. de Souza, J. Chem. Soc. Dalton Trans., (1987) 2955.
9 A.G. de Souza and C. Airoldi, Thermochim. Acta, 130 (1988) 95.
10 C. Airoldi and A.G. de Souza, J. Chem. Thermodyn. 21 (1989) 283.
11 A.G. de Souza, J.H. de Souza and C. Airoldi, J. Chem. Soc. Dalton Trans., (1991) 1751.
12 S.J. Ascroft, J. Chem. Soc. A, (1970) 1020.
13 S.J. Ascroft, J. Chem. Eng. Data, 33 (1988) 73.
14 C. Airoldi and E.A. Digiamprietri, J. Chem. Thermodyn, 24 (1992) 33.
15 J.C. Bailar, Jr. and P.F. Cundy, Inorg. Synth., 1 (1939) 104.
16 J.W. George, Progr. Inorg. Chem., 2 (1960) 33.
17 A.I. Vogel, A Text-Book of Quantitative Inorganic Analysis, Pergamon, Oxford, 1973.
18 A.J. Aarts, H.O. Desseyn and M.A. Herman, Transition Met. Chem., 3 (1978) 144.
19 L.P. Battaglia, A.B. Corradi, G. Marcotrigiano and G.C. Pellacani, J. Chem. Soc. Dalton Trans., (1979) 1089.
20 A.O. Baghlaf, M. Ishaq, O.A.S. Ahmed and M.A. Al-Julani, Polyhedron, 4 (1985) 853.
21 M.A. Baldwin, A.M. Kirkien, A.G. Loudon and A. MacColl, Org. Mass Spectrom., 4 (1970) 81.
22 C. Airoldi, M.L.C.P. Silva and A.P. Chagas, J. Chem. Soc. Dalton Trans., (1986) 1913.
23 D.D. Wagman, W.H. Evans, V.B. Parker, R.H. Schumm, I. Halow, S.W. Bailey, K.L. Churney and R.L. Nuttall, J. Phys. Chem. Ref. Data, 11 (1982) Suppl. 2.
24 D. Cubicciotti, Inorg. Chem., 7 (1968) 211.
25 S. Inagari, S. Murata and M. Sakiyama, Bull. Chem. Soc. Jpn., 55 (1982) 2808.
26 D. Cubicciotti and H. Eding, J. Phys. Chem., 69 (1965) 3621.