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Thermochimica Acta 292 (1997) 71–75

thermochimica
acta

Thermochemical properties of complexes of thiourea and tetramethylthiourea with antimony and bismuth tribromides

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Received 30 October 1995; received in revised form 19 July 1996; accepted 9 September 1996

Abstract

The new adducts $M\mathrm{Br}_3{\cdot}L$ (where M = Sb or Bi; L = thiourea (TU) or tetramethylthiourea (TMTU)), were synthesized, characterized by elemental analysis, melting temperatures, thermogravimetry, IR spectroscopy and mass spectra. The solution–reaction calorimetry was used to determine the enthalpy of formation at 298.15 K of crystalline $\mathrm{SbBr_3{\cdot}TMTU} = -160.0$, $\mathrm{BiBr_3{\cdot}TMTU} = -207.0$, $\mathrm{SbBr_3{\cdot}TU} = -208.6$, and $\mathrm{BiBr_3{\cdot}TU} = -256.0\ \mathrm{kJ\ mol^{-1}}$. The mean metal–sulphur bond enthalpies for the same sequence were calculated: 123.0, 153.0, 120.7, and 151.2 $\mathrm{kJ\ mol^{-1}}$. The standard enthalpies of decomposition of the complexes as well as the lattice standard enthalpies and the Lewis acid/base reactions in the gaseous phase were calculated through adequate thermochemical cycles. © 1997 Elsevier Science B.V.

Keywords: Antimony; Bismuth; Calorimetry; Tetramethylthiourea; Thermochemistry

1. Introduction

Synthesis, characterization and thermochemical studies have been performed for complexes of tetramethylthiourea [1], *N,N*-dimethylthioacetamide and *N,N*-dimethylthioformamide [2], thiourea and thioacetamide [3] with antimony and bismuth triiodides. The thermochemical studies involving these adducts have enabled the determination of some energetic parameters such as the standard enthalpies of formation and enthalpies of dissociation of element–ligand bonds, which are important for evaluating the nature of the participation of the ligand in forming element–ligand bond in adducts and chelates [1–7]. 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 [8].

Structures involving amides and thioamides show a great tendency of these ligands to bond to the acceptor via oxygen [9] or sulphur [10,11] donor atoms of these molecules. However, in rare cases, nitrogen can act as lewis base centre to bond the metal atom [12,13].

In this paper the synthesis, characterization and calorimetric measurements of complexes of antimony and bismuth tribromides with thiourea (TU) and tetrametilthiourea (TMTU) are reported.

2. Experimental

2.1. Chemicals

Solvents used in all preparation work were distilled and kept dry. The TU and TMTU were used without

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PII S0040-6031(96)03085-7

further purification. A mixture of methanol with hydrochloric acid was shown to be very suitable in dissolving the reagents and the adducts in calorimetric measurements.

2.2. *Preparations*

The antimony and bismuth tribromides were prepared as described in the literature [1,14]. The complex $SbBr_3$·TMTU was prepared through the slow addition of tetramethylthiourea to $SbBr_3$, in a 1 : 1 molar ratio, in CS_2 as solvent, under anhydrous conditions. Stirring was maintained for 3 h. After removal of the solvent, the yellow solid formed was washed with CS_2 and dried in vacuo. The complexes $SbBr_3$·TU, $BiBr_3$·TMTU and $BiBr_3$·TU, were synthesized analogously. The yields in all preparations were in the 81–86% range. Microanalysis for bromide, carbon, hydrogen and nitrogen were within the error of the values expected from the established formula.

2.3. *Calorimetric measurements*

The reaction–solution calorimetric measurements were performed in an LKB 8700-1 isoperibolic precision calorimeter system [15]. Ampoules containing 5–50 mg of substrate were prepared in an dry-box and broken into the glass reaction vessel charged with $0.10\ dm^3$ of calorimetric solvent at 298.15±0.02 K. Details of the operational procedure and the method for calculation of the accuracy of the instrument have been already described earlier [16]. For each determination the uncertainty interval is quoted as twice the standard deviation of the mean.

2.4. *Other measurements*

The melting temperatures for all compounds were determined using a MICROQUIMICA model MQAPF-301 apparatus. Infrared spectra were recorded on Nujol mulls with a BOMEM model MB-102 spectrophotometer. Thermogravimetric curves were obtained in a dynamic atmosphere of nitrogen using a SHIMADZU model TG-50 thermobalance, with samples varying in weight from 2 to 3 mg and a heating rate of $0.16\ K\ s^{-1}$. A Hewlett–Packard model 59988-A spectrometer was used for obtaining ligand and adduct mass spectra with 70 eV (approx. 1.12×10^{-17} J) ionization energy at 523 K.

3. Results and discussion

The melting temperatures of the adducts of antimony and bismuth are shown in Table 1. The results of elemental analysis of the complexes are in complete agreement with the general formula, as shown in Table 1.

The infrared spectra of the adducts showed a decrease of the CS stretching frequency by comparison with the free ligands, from 730 (TU) [17] and $1126\ cm^{-1}$ (TMTU) [18] to 705 and $1115\ cm^{-1}$, for the Sb adducts and to 708 and $1060\ cm^{-1}$ for the Bi adducts, respectively. The opposite behaviour was observed for the CN stretching frequency: from 1425 (TU) [17] and $1504\ cm^{-1}$ (TMTU) [18] in the free ligands to 1435 and $1585\ cm^{-1}$ for the antimony adducts and 1432 and $1586\ cm^{-1}$ for the bismuth adducts, respectively. These shifts indicate M–S bond formation in these complexes [1–3,7,18,19].

The mass spectra of the adducts, did not show the parent ion. However, some fragments relating to tribromides, i.e. $[MBr_3]^+$, $[MBr_2]^+$, $[MBr]^+$, $[M]^+$, $[Br_2]^+$ and $[Br]^+$ were detected. These peaks were enriched by the fragments originating from the ligands: $[(CH_3)_4NCN]^+$, $[(CH_3)_3CSN]^+$, $[HCSN(CH_3)]^+$, $[CH_3CSNH]^+$ or $[(CH_3)_2CS]^+$,

Table 1
Mass percentage analysis (obtained values in parentheses) and melting temperatures

Compound	Analysis (%)				Temperature (K)
	Br	C	H	N	
$SbBr_3$·TU	53.7 (54.8)	2.6 (2.7)	6.2 (6.4)	6.2 (6.4)	363
$SbBr_3$·TMTU	47.3 (48.0)	11.7 (12.0)	0.7 (0.9)	5.3 (5.6)	370
$BiBr_3$·TU	46.0 (45.7)	2.5 (2.3)	0.9 (0.8)	5.0 (5.3)	379
$BiBr_3$·TMTU	40.6 (41.3)	10.0 (10.3)	1.9 (2.1)	4.9 (4.8)	386

$[CH_3CSN]^+$, $[SCCH_2]^+$, $[SCN]^+$, $[CS]^+$ or $[HNC_2H_5]^+$ or $[N(CH_3)d_2]^+$, $[NC_2H_5]^+$ and $[C_2H_4N]^+$ to the TMTU and $[H_4N_2CS]^+$, $[H_2NCS]^+$, $[SCN]^+$, $[N(CH_3)_2]^+$ or $[H_6NC_2]^+$, $[H_2N_2C]^+$ and $[HN_2C]^+$ to the TU. Similar fragmentation was observed for adducts with transition metal and similar ligands [23,24].

The thermogravimetric results for TMTU showed loss of mass below the melting point; however, for TU complexes the loss of mass could be observed above the melting point. The thermogravimetry curves for $SbBr_3{\cdot}TMTU$ and $SbBr_3{\cdot}TU$ occurred in two distinct steps of decomposition: in the first step, the ligand and 3Br were eliminated in the range from 369 to 553 K and from 553 to 703 K, respectively; the second step in the range from 364 to 545 K and from 545 to 728 K, respectively, corresponding to volatilization of the metal. For bismuth compounds, a complete weight loss of mass was observed in only one step in the range from 387 to 735 K and from 379 to 722 K, respectively. These results enable establishing the thermal stability in the following order: $BiBr_3{\cdot}TMTU > SbBr_3{\cdot}TMTU > BiBr_3{\cdot}TU > SbBr_3{\cdot}TU$.

The standard molar enthalpy of reaction $(\Delta_r H^0_m)$ was obtained at 298.15 K from the reaction–solution enthalpies $(\Delta_i H^0_m)$ of each reagent and product dissolved sequentially in a solution of MeOH + HCl as calorimetric solvent (Table 2) for the following reaction [1–5]:

$$MBr_3\,(cr) + L\,(cr) \rightarrow MBr_3 \cdot L\,(cr);\ \Delta_r H^0_m$$

The $\Delta_r H^0_m$ values were derived from these tabulated values by applying a convenient thermochemical cycle. Then,

$$\Delta_r H^0_m = \Delta_1 H^0_m + \Delta_2 H^0_m - \Delta_3 H^0_m \qquad (1)$$

Relevant data are listed in Table 3, and are useful for comparing the acidity of metal bromides [20] and for calculating the standard molar enthalpies of formation $(\Delta_f H^0_m\,(cr))$ of the crystalline adducts (Table 3) were determined from $\Delta_r H^0_m$ and the standard molar enthalpies of formation of reactants [7] in the established reaction, as shown in Table 4.

The standard molar enthalpies of complex decomposition $(\Delta_D H^0_m)$ give ligands or ligands plus metal tribromides in the gasesous phase [1–5] as represented by expressions:

$$MBr_3 \cdot L\,(cr) = MBr_3\,(cr) + L\,(g);\ \Delta_D H^0_m \qquad (2)$$

$$MBr_3 \cdot L\,(cr) = MBr_3\,(g) + L\,(g);\ \Delta_M H^0_m \qquad (3)$$

can be calculated by means of the expressions:

$$\Delta_D H^0_m = -\Delta_r H^0_m + \Delta^g_{cr} H^0_m\,(L) \qquad (4)$$

$$\Delta_M H^0_m = -\Delta_D H^0_m + \Delta^g_{cr} H^0_m\,(MBr_3) \qquad (5)$$

From the enthalpies of sublimation of TU [26] and TMTU [25] and also of $SbBr_3$ and $BiBr_3$ [27], listed in Table 4, the values of $\Delta_D H^0_m$ and $\Delta_M H^0_m$ were derived (Table 3).

Table 2
Standard molar enthalpies (kJ mol^{-1}) of solution and reaction, at 298.15 K

No.	Reactant	Solvent [a]	Solution	No. of expts.	$\Delta_i H^0_m$
1	$SbBr_3$ (cr)	S_1	A_1	5	23.19±0.09
2	TU (cr)	A_1	A_2	6	69.89±0.27
3	$SbBr_3{\cdot}TU$ (cr)	S_1	A_2	5	112.08±0.31
4	$SbBr_3$ (cr)	S_1	B_1	5	23.19±0.09
5	TMTU (cr)	B_1	B_2	6	25.85±0.10
6	$SbBr_3{\cdot}TMTU$ (cr)	S_1	B_2	6	70.35±0.30
7	$BiBr_3$ (cr)	S_2	C_1	5	20.35±0.08
8	TU (cr)	C_1	C_2	5	67.41±0.19
9	$BiBr_3{\cdot}TU$ (cr)	S_2	C_2	7	104.63±0.40
10	$BiBr_3$ (cr)	S_2	C_1	5	20.19±0.07
11	TMTU (cr)	C_1	C_2	7	27.33±0.13
12	$BiBr_3{\cdot}TMTU$ (cr)	S_2	C_2	6	66.21±0.24

[a] The calorimetric solvent used were MeOH + HCl (aq. 1.2 mol dm^{-3})=[S_1] and MeOH + HCl (aq. 1.0 mol dm^{-3})=[S_2].

Table 3
Standard molar enthalpies (in kJ mol^{-1}) for the adducts

	$SbBr_3{\cdot}TU$	$SbBr_3{\cdot}TMTU$	$BiBr_3{\cdot}TU$	$BiBr_3{\cdot}TMTU$
$\Delta_r H_m^0$	-19.01 ± 0.42	-21.31 ± 0.33	-16.87 ± 0.45	-19.69 ± 0.24
$\Delta_f H_m^0$ (cr)	−208.6	−160.0	−256.0	−207.0
$\Delta_D H_m^0$	131.0	104.6	128.9	102.0
$\Delta_M H_m^0$	−193.4	−162.4	−229.4	−198.9
$\Delta_f H_m^0$ (g)	−120.7	−123.0	−151.2	−153.0
$\langle D\rangle(M\text{–}S)$	120.7	123.0	151.2	153.0

Table 4
Auxiliary data (in kJ mol^{-1})

Compound	$\Delta_f H_m^0$(cr)	$\Delta_{cr}^{g} H_m^0$
$SbBr_3$ (cr)	−100.4	101.7
$BiBr_3$ (cr)	−150.0	134.3
TU (cr)	-89.15 ± 0.50	112.0 ± 1.5
TMTU (cr)	-38.3 ± 2.3	83.26 ± 0.20

All attempts to measure directly the thermochemical parameters for the adducts in the gasesous phase were unsuccessful due to the difficulty in subliming the adducts. However, the standard molar enthalpy in gaseous phase, $\Delta_f H_m^0$ (g), must be derived from reaction:

$$MBr_3 \cdot L\,(g) = MBr_3\,(g) + L\,(g);\ \ \Delta_g H_m^0 \qquad (6)$$

and calculated by the expression:

$$\Delta_f H_m^0\,(g) = \Delta_M H_m^0 - \Delta_{cr}^{g} H_m^0 \qquad (7)$$

where $\Delta_{cr}^{g} H_m^0$ is the standard molar enthalpy of sublimation of the complex [1–5]. The mean M–S bond enthalpy, $\langle D\rangle(M\text{–}S)$, depends on the enthalpy of sublimation of the compound, which is shown to be unstable during the heating process. Based on the assumption that $\Delta_{cr}^{g} H_m^0$ (adduct) = $\Delta_{cr}^{g} H_m^0$ (ligand), for which the validity of this hypothesis is shown to be reasonable within ±10 kJ mol^{-1} for some sublimable adducts [21,22], $\Delta_f H_m^0(g)$ was calculated and, consequently, the value of $\langle D\rangle(M\text{–}S)$ was determined by means of the expression:

$$\langle D\rangle(M\text{–}S) = [\Delta_f H_m^0(g)]/n \qquad (8)$$

where $n=1$. These results are listed in Table 3.

The results of standard molar enthalpy of formation of complexes in the condensed state showed no substantial difference between the ligands TMTU and TU, hence of the adducts $SbBr_3{\cdot}TMTU$ and $SbBr_3{\cdot}TU$, and the adducts of bismuth. This shows that the substitution of hydrogen by methyl group was not promising. Only $AsBr_3{\cdot}TMTU$ [1] had the value of 15 kJ mol^{-1} and above. As to order of acidity of tribromides of As, Sb and Bi, it is $AsBr_3 > SbBr_3 > BiBr_3$ with the same stoichiometry. Nevertheless, as to relative basicity in general we obtain TMTU > TU, with the exception of $AsBr_3{\cdot}TU$ [1], because it has a different stoichiometry [1,2,5]. However, the values of $\Delta_f H_m^0$ (cr), show that: $AsBr_3{\cdot}TMTU > BiBr_3{\cdot}TMTU > SbBr_3{\cdot}TMTU$ and $BiBr_3{\cdot}TU > SbBr_3{\cdot}TU$. This does not correspond to earlier results, which says, $BiBr_3 > SbBr_3$. Consequently, the values of mean metal–sulphur bond enthalpies $\langle D\rangle(M\text{–}S)$, i.e. $BiBr_3{\cdot}TMTU > SbBr_3{\cdot}TU > AsBr_3{\cdot}TMTU$, that show the inverse of results of $\Delta_r H_m^0$ and $BiBr_3{\cdot}TU > SbBr_3{\cdot}TU$, disagree with the values of $\Delta_r H_m^0$; we believe that TU is a better donor of electrons with $BiBr_3$ than $SbBr_3$. Thus, TMTU and TU has the same tendency [1–5].

4. List of abbreviations

Name	Symbol
Thiourea	TU
Tetramethylthiourea	TMTU
Standard molar enthalpy reaction–solution	$\Delta_i H_m^0$
Standard molar enthalpy of reaction	$\Delta_r H_m^0$
Standard molar enthalpy of formation in solid phase	$\Delta_f H_m^0$(cr)
Standard molar enthalpy in gasesous phase	$\Delta_f H_m^0$(g)
Standard molar lattice enthalpy	$\Delta_M H_m^0$
Standard molar enthalpy of decomposition	$\Delta_D H_m^0$

Standard molar enthalpy of sublimation	$\Delta_{\mathrm{cr}}^{\mathrm{g}}H_{\mathrm{m}}^{0}$
Mean M–S bond enthalpy	$\langle \mathrm{D}\rangle(M\text{–S})$

Acknowledgements

The authors thank the Conselho Nacional de Desenvolvimento Científico e Tecnológico (CNPq) and the Programa de Apoio ao Desenvolvimento Científico e Tecnológico (PADCT) for financial support of this work, and also Dr. Claudio Airoldi (UNICAMP) for providing the facility for obtaining the solution–reaction calorimetric measurements.

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