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THERMOCHEMICAL PARAMETERS OF COMPLEXES OF DI-ISOBUTYLDITHIOCARBAMATE WITH PHOSPHORUS-GROUP ELEMENTS

A. G. de Souza[*a], *Fe. de Souza Neto*[a], *J. H. de Souza*[a], *R. O. Macedo*[a], *J. B. L. de Oliveira*[a] *and C. D. Pinheiro*[b]

[a]Departamento de Química, Centro de Ciências Exatas e da Natureza, Universidade Federal da Paraíba, 58059-900, Joo Pessoa, Paraíba
[b]Departamento de Ciências Exatas e da Natureza, Centro de Formaçâo de Professores, Universidade Federal da Paraíba, 58900-000, Cajazeiras, Paraíba, Brazil

Abstract

The standard molar enthalpy of formation of crystalline di-isobutyldithiocarbamate complexes of P, As, Sb and Bi(III) has been derived by solution calorimetry at 298.15 K. The corresponding standard molar enthalpies of sublimation were estimated by means of differential scanning calorimetry. From the standard molar enthalpies of formation of the gaseous chelates the homolytic and heterolytic mean metal-sulphur bond-dissociation enthalpies were calculated.

Keywords: bismuth, calorimetry, dithiocarbamate, enthalpy, phosphorous

Introduction

In spite of the large number of publications concerned with the structural features of these compounds, the first thermochemical results appeared only at the end sixties [1] and the first review including thermal data and solution thermochemistry of metal dithiocarbamate complexes and related compounds was published at the beginning of the eighty decade [2, 3], followed by another recent review [4].

The enthalpies of formation of chelates of di-*n*-propyl, di-*n*-butyl and di-isobutyldithiocarbamate of Zn(II), Cd(II) and Hg(II) in the solid state have been obtained by solution-reaction calorimetry. From the thermochemical properties of these chelates in the gaseous phase, the enthapies of the metal-sulphur bonds have been derived [5–7].

Experimental

Preparations

Tris(di-isobutyldithiocarbamate) of P(III), As(III), Sb(III) and Bi(III) were prepared by slowly adding a solution of di-isobutylammonium di-isobutyldithiocar-

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[*] Author to whom all correspondence should be addressed.

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bamate in acetone to a stirred solution of the metal chloride in acetone in 1:3 molar proportions [8]. The crystals were isolated, recrystallized from acetone and dried in vacuo, with yields in the range 80–87%. Microanalysis for carbon, hydrogen and nitrogen were within experimental error of the expected values from the established formulas.

Other measurements

The melting temperatures for all compounds were determined by means of a MICROQUIMICA 301 apparatus. Thermogravimetric curves were obtained using a SHIMADZU model TGA-50 thermobalance, at a heating rate of 0.17 K s^{-1} in a dry nitrogen flux of 0.33 cm^3 s^{-1}. Infrared spectra were recorded as KBr pellets on a BOMEM model MB-102 spectrophotometer, mass spectra of the ligand and chelates on a Hewlett-Packard model 5988A spectrometer with an ionization energy of 70 eV.

An LKB 8700-1 isoperibolic precision calorimeter system was used for all solution-reaction measurements. Details of the operational procedure, calculation method and accuracy of the instrument are as described before [7, 8]. The enthalpies of fusion, and the heat capacities of the solid and liquid forms of the chelates were determined in a SHIMADZU model DSC-50 differential scanning calorimeter, purged with dry nitrogen [9]. For each determination the uncertainty interval is quoted as twice the standard deviation of the mean.

Results and discussion

The tris(di-isobutyldithiocarbamate) of P(III), As(III), Sb(III) and Bi(III) chelates showed narrow melting ranges, 395–397, 403–406, 380–381 and 570–571 K, respectively, in good agreement with those reported [10, 11]. The mode of coordination of the dialkyldithiocarbamate and the small intervals of melting suggest the existence of very stable compounds. However, on cooling the melting sample and heating again the previous melting-point interval was not reproduced. Microanalytical data for chelates were within experimental error of the expected values from the established formula.

The νCN band assumes a double-band character which is reflected in the appearance of a stretching band shifted to higher frequency: 1464, 1475, 1485 and 1455 cm^{-1} for P, As, Sb and Bi(III), respectively. For all complexes this band frequency is higher than that of the respective ligand. On the other hand, a decrease in the ν_{CS} stretching band is observed and an isolated band near 1000 cm^{-1} indicates that the ligand is bonded in a bidentate manner to metal [12–14]: 1062, 1090, 1090 and 1090 cm^{-1} for P, As, Sb and Bi(III), respectively. The mass spectra of the complexes did not reveal the presence of the parent ions. The thermogravimetric curves showed loss of mass before the melting temperature for phosphorus and arsenic and after for antimony and bismuth chelates.

The standard molar enthalpy of reaction, $\Delta_r H^o_m$, was obtained, at 298.15 K, from the reaction-solution enthalpies, $\Delta_i H^o_m$, of each reagent and product dissolved sequentially in acetone (Table 1) for the following reaction [9, 15, 16]:

$$ECl_{3(l)} + 3NH_2Bu^i_2S_2CNBu^i_{2(cr)} \rightarrow E(S_2CNBu^i_2)_{3(cr)} + 3NH_2Bu^i_2Cl_{(cr)},\ \Delta_r H^o_m \quad (1)$$

The $\Delta_r H^o_m$, values were derived from these tabulated values by applying a convenient thermochemical cycle, relevant data being listed in Table 2.

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

i	Reactant	Solvent	Solution	N° of expts.	$\Delta_r H^o_m$
01	$3Bu^i_2NH_2S_2CNBu^i_{2(cr)}$	Acetone	A1	6	40.30±0.01
02	$PCl_{3(l)}$	A1	A2	6	-407.76±1.33
03	$P(S_2CNBU^i_2)_{3(cr)}$	Acetone	A3	6	47.66±0.20
04	$3Bu^i_2NH_2Cl_{(cr)}$	A3	A4	6	13.29±0.28
05	$AsCl_{3(l)}$	Acetone	B1	6	-7.07±0.01
06	$3Bu^i_2NH_2S_2CNBu^i_{2(cr)}$	B1	B2	6	-31.33±0.05
07	$As(S_2CNBu^i_2)_{3(cr)}$	Acetone	B3	6	41.60±0.15
08	$3Bu^i_2NH_2Cl_{(cr)}$	B3	B4	6	21.15±0.02
09	$SbCl_{3(cr)}$	Acetone	C1	6	-24.26±0.04
10	$3Bu^i_2NH_2S_2CNBu^i_{2(cr)}$	C1	C2	6	-31.83±0.07
11	$3Bu^i_2NH_2Cl_{(cr)}$	Acetone	C3	6	15.41±0.09
12	$Sb(S_2CNBu^i_2)_{3(cr)}$	C3	C4	6	40.96±0.33
13	$BiCl_{3(cr)}$	Acetone	D1	6	-30.42±0.74
14	$3Bu^i_2NH_2S_2CNBu^i_{2(cr)}$	D1	D2	6	-28.01±0.09
15	$Bi(S_2CNBu^i_2)_{3(cr)}$	Acetone	D3	6	37.73±0.82
16	$3Bu^i_2NH_2Cl_{(cr)}$	D3	D4	6	13.22±0.11

The standard molar enthalpies of formation of the crystalline chelates (Table 2) were determined from $\Delta_r H^o_m$ and the standard molar enthalpies of formation of the metal chlorides [17], ligand [18] and ammonium chloride [19], using expression (2), for which data were listed in Table 3.

$$\Delta_f H^o_m[E(S_2CNBu^i_2)_3]_{(cr)} = \Delta_r H^o_m - 3\Delta_f H^o_m(NH_2Bu^i_2Cl)_{(cr)} +$$
$$+ \Delta_f H^o_m(ECl_3)_{(cr)} + 3\Delta_f H^o_m(NH_2Bu^i_2S_2CNBu^i_2)_{(cr)} \quad (2)$$

The standard molar enthalpies of sublimation, $\Delta^g_{cr} H^o_m$, were determined by means of differential scanning calorimetry and estimative methods [7, 16]. The molar standard enthalpies of fusion, $\Delta^l_{cr} H^o_m$, were obtained (Table 2). The molar standard enthalpies of vaporization were estimated [7, 15, 16], Table 2. The heat capacities for the solid and liquid phases of the complexes were determined for DSC. However, for the gas phase these quantities were estimated [16, 21]. The values obtained are listed in Table 2, together with the standard molar enthalpies of sublimation, which were calculated by applying all these auxiliary data in the expression

Table 2 Standard molar enthalpies (kJ mol^{-1}), heat capacities (kJ mol^{-1} K^{-1}) and temperatures (K) for the chelates

Parameters	$P(S_2CNBu^i_2)_3$	$As(S_2CNBu^i_2)_3$	$Sb(S_2CNBu^i_2)_3$	$Bi(S_2CNBu^i_2)_3$
$-\Delta_r H^o_m$	374.39±1.37	206.11±0.15	206.94±0.35	191.84±1.11
$-\Delta_f H^o_m(cr)$	702.28±4.67	519.30±4.57	597.30±4.55	579.13±4.59
$\Delta^l_{cr} H^o_m$	28.43±0.62	25.12±0.81	44.23±1.02	47.96±2.6
$\Delta^g_l H^o_m$	45.1±2.2	49.6±2.4	55.4±3.7	58.6±2.9
T_{fus}	383.70	402.39	373.88	382.82
T_{vap}	486.76	534.56	579.44	585.30
$C_{p,m}(cr)$	1.26±0.21	0.84±0.01	1.66±0.05	0.84±0.09
$C_{p,m}(l)$	1.40±0.15	1.44±0.09	1.64±0.06	0.62±0.13
$C_{p,m}(g)$	1.10±0.01	1.09±0.03	1.44±0.02	0.60±0.44
$\Delta^g_{cr} H^o_m$	138±3	128±2	157±3	147±3
$-\Delta_f H^o_m(g)$	564.28±5.55	425.30±4.98	440.30±5.46	432.13±5.48
$-\Delta_{ho} H^o_m$	1141.4±23.5	989.3±23.3	965.1±23.4	901.7±23.4
$\Delta_{he} H^o_m$	6385.7±23.5	5886.7±23.3	5252.6±23.4	5097.4±23.5
$<D>(E–S)$	190±3.9	164.8±3.8	160.8±3.9	150.3±3.9
$<D'>(E–S)$	1064.2±3.9	981.1±3.8	875.4±3.9	849.9±3.9

sion (3) and consequently the standard molar enthalpies of formation in the gas phase, listed in Table 2, were calculated.

$$\Delta^g_{cr} H^o_m = \int_{298K}^{T_{fus}} C_p(s)dT + \Delta^l_{cr} H^o_m + \int_{T_{fus}}^{T_{vap}} C_p(l)dT + \Delta^g_l H^o_m + \int_{T_{vap}}^{T_{298K}} C_p(g)dT \tag{3}$$

From the auxiliary data listed in the Table 3, one can calculate the mean enthalpy of metal–sulphur bond for homolytic, $<D>(E–S) = -\Delta_{ho} H^o_m/6$ and for heterolytic, $<D'>(E–S) = -\Delta_{he} H^o_m/6$. In these determinations the reorganization energy associated with the ligand upon complexation is neglected and assuming an equivalence of all metal–sulphur bond, even though for these complexes the metallic atoms are expected to be anisobidentately bonded by the sulphur atoms [5–9, 15, 16].

Conclusion

An abstract decrease in $<D>$ (E–S) values was observed from phosphorous to bismuth. Therefore, the larger $<D>$(P–S) value was interpreted as a better overlap of *d* orbitals of P and S atoms in bonding. The less effective π bonding in the Bi–S bond, as a consequence of the increase of the hardness of the Bi atom, caused a de-

Table 3 Auxiliary data (kJ mol^{-1})

Compound	$-\Delta_f H^\circ_m$	Ref.
$PCl_{3(l)}$	319.7±0.3	[17]
$AsCl_{3(l)}$	305.0±2.2	[17]
$SbCl_{3(cr)}$	382.17±0.06	[17]
$BiCl_{3(cr)}$	379.1±0.1	[17]
$Bu^i_2NH_2S_2CNBu^i_{2(cr)}$	463.8±1.4	[18]
$Bu^i_2NH_2Cl_{(cr)}$	461.07±0.50	[19]
$P_{(g)}$	–314.6±0.2	[17]
$As_{(g)}$	–302.5±0.2	[17]
$Sb_{(g)}$	–262.3±0.1	[17]
$Bi_{(g)}$	–207.1±0.1	[17]
$P^{3+}_{(g)}$	–6160.1±0.1	[17]
$As^{3+}_{(g)}$	–5801.1±0.1	[17]
$Sb^{3+}_{(g)}$	–5151.0±0.4	[17]
$Bi^{3+}_{(g)}$	–5004.0±1.7	[17]
$Bu^i_2NCS^{*}_{2(g)}$	–87.50±7.60	[22]
$Bu^i_2NCS^{-}_{2(g)}$	112.9±7.6	[7]

crease of <D>(Bi–S). Similar behavior was observed for diethyl- and di-*n*-butyldithiocarbamates of P, As, Sb and Bi [9, 15, 16].

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