Mean Phosphorus- and Arsenic–Sulphur Bond Enthalpies in Diethyldithiocarbamate Chelate Complexes

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The standard enthalpies of formation at 298.15 K of crystalline tris(diethyldithiocarbamate) compounds of P and As were determined by solution-reaction calorimetry, giving -304.5 ± 7.6 and -104.5 ± 7.6 kJ mol^{-1} respectively. The enthalpies of sublimation, 143 ± 2 and 124 ± 3 kJ mol^{-1} respectively, were estimated. From these values, the enthalpies of formation of both compounds in the gaseous phase were derived. The homolytic and heterolytic phosphorus- and arsenic–sulphur bond-enthalpy parameters were calculated. The larger values for phosphorus are interpreted as the result of a better overlap of the *d* orbitals of the atoms involved.

The abundant literature dealing with the chemistry, properties, molecular structures, and electronic properties of sulphur complexes has been extensively reviewed.[1–3] Among the ligands, dithioacid derivatives play a notable role, not only in the coordination features, but also in many technical applications.[2] For example, a recent review of the analytical chemistry of metal dithiocarbamate complexes, covering the literature up to the beginning of 1983, reports some interesting topics on metal determinations by means of several traditional analytical methods[4] and new methods for trace metal determinations in foods, pharmaceutical products, and environmental and biological samples.

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 of sixties[5] and the first review including thermal data and solution thermochemistry of metal dithiocarbamate complexes and related compounds was published at the beginning of this decade,[6] followed by another recent revision.[7]

From the standard enthalpy of formation of the complexes $[M(S_2CNH_2)_2]$ (M = Zn, Cd, or Pb), determined by solution calorimetry, the homolytic and heterolytic metal–sulphur bond enthalpies were estimated[5] for the chelates. These parameters have recently been re-estimated by the group-additivity method for the zinc and cadmium complexes.[8] The standard enthalpy of formation of tris(diethyldithiocarbamato)iron(III) in the solid state has also been determined by solution calorimetry.[9] The same procedure was applied to the bis chelates of nickel[10] and copper,[11] and the metal–sulphur bond enthalpies were derived. These last two systems were studied by means of ligand-exchange reactions involving the displacement of pentane-2,4-dionate by diethyldithiocarbamate.

The thermodynamic data show that dialkyldithiocarbamate complexes of cadmium have a tendency to dimerise in benzene solution, however this behaviour was not observed for similar zinc complexes.[12] These complexes display acid properties since they react with primary and secondary amines and pyridine in 1:1 molar ratios.[12]

The mean zinc–sulphur bond enthalpy in bis(diethyldithiocarbamato)zinc(II) has recently been determined.[8] After recalculating the same parameters for the nickel and copper complexes from data in previous publications, the resulting thermochemical values were found to correlate with the metal–sulphur bond distances.[8]

This paper deals with phosphorus and arsenic compounds of diethyldithiocarbamate, which have previously been studied only from the point of view of their structural chemistry.[1] Here, the first thermochemical results for the tris(diethyldithiocarbamates) of P and As are reported. The difference in the element–sulphur mean standard enthalpies for these compounds suggests that there is a better participation of the *d* orbitals in the phosphorus–sulphur bonds.

Experimental

Chemicals.—The solvents used in the preparations, the reagents PCl_3 (Fischer) and $AsCl_3$ (Carlo Erba), and calorimetric solvents were carefully dried and distilled prior to use. Acetone was chosen as the calorimetric solvent due to its ability to dissolve the chlorides, salts, and chelates. The salts and chelates were rigorously dried *in vacuo* before preparing the ampoules and a dry-box was used for air-sensitive compounds.[13]

Preparations.—All operations involved in the preparations and purifications were carried out either *in vacuo* or in a dry-box under an atmosphere of dried nitrogen.[14]

The salts diethylammonium chloride and diethylammonium diethyldithiocarbamate were synthesised.[8] Their analyses and melting points were in complete agreement with their formulation and reported melting points.[8]

A previously reported procedure[15] for the phosphorus and arsenic compounds was slightly modified. Some details for the phosphorus compound will be briefly described. Under anhydrous conditions and a flux of dry nitrogen, phosphorus chloride (16.10 mmol) was added dropwise to a mechanically stirred mixture of light petroleum (200 cm^3) containing carbon disulphide (48.50 mmol) and diethylamine (*ca.* 110 mmol) with the reaction flask immersed in a carbon dioxide–acetone bath. White ethylamine hydrochloride was formed immediately in a very exothermic reaction. After the addition, the mixture was stirred for 1 h at room temperature and then refluxed for approximately 2 h. After cooling the solid was filtered off and half of the solvent was pumped off. The remaining solution was allowed to stand overnight in a refrigerator at 4 °C. The resulting yellow solid was recrystallised from carbon tetrachloride and dried *in vacuo*. Yield 60%. The arsenic compound was obtained similarly in 70% yield, starting from arsenic chloride (35.79 mmol), carbon disulphide (107.40 mmol), and diethylamine (214.80 mmol) in light petroleum (200 cm^3).

Calorimetry.—The reaction and solution enthalpies were measured in an LKB 8700-1 isoperibolic calorimeter system. The details of the experimental procedure and the data processing have been described previously.[16] The enthalpy of fusion, and the heat capacities of the solid and liquid forms of the compounds, were determined in a Perkin-Elmer dsc-2 differential scanning calorimeter.[17] The uncertainty intervals for each determination are quoted as twice the standard deviation of the mean.

Other Measurements.—Thermogravimetric curves were obtained in a dynamic atmosphere of nitrogen, in the range 30—700 °C, using a Perkin-Elmer model TGS-1 thermobalance with a programmed heating rate of 5.0 °C min^{-1}. Melting points for air-sensitive compounds were determined in sealed capillary tubes with a Unimelt capillary point apparatus. The melting points of the compounds were measured by a Reichert Termopan ultramicroscope with a programmed heating rate of 3 °C min^{-1}. A Finnigan 1015 S/L spectrometer was used to obtain the mass spectra. Infrared spectra were obtained for sample mulls in Fluorolube and Nujol on a Perkin-Elmer 399 B spectrophotometer.[17]

Results and Discussion

The phosphorus and aresenic compounds showed narrow melting ranges, 404—405 and 416—417 K, respectively. The mode of co-ordination 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.[18]

The thermogravimetric results demonstrated that the phosphorus compound started to decompose before the melting point (372 K). Although three stages of decomposition can be delineated in the thermogravimetric curve, the inflections are not very well defined, indicating the occurrence of several simultaneous reactions.[18] However, the loss of mass (62.0%) in the first step in the range 370—413 K corresponds to the loss of $2S_2CNEt_2$, followed by $CNEt_2$ in the range 413—569 K, and finally the decomposition of phosphorus sulphide (P_2S_5 and P_4S_7) in the range 568—871 K, leaving a residue of 7.0%. For the arsenic compound only two distinct steps were observed. In the first step S_2CNEt_2 plus $2SCNEt_2$ were eliminated in the range 495—522 K, followed by the sublimation of sulphides (AsS_2 or As_2S_3) in the range 523—627 K.[19] The total weight loss observed in these thermogravimetric curves confirmed the stoicheiometries of the compounds, which had been established by elemental analysis.

The mode of co-ordination of the chelates mainly affects the C–N and C–S stretching bands.[20] Diethylidithiocarbamate anion has C–N stretching frequencies at 1 480 and 1 465 cm^{-1} in its sodium and in diethylammonium salts, respectively. This band indicates a considerable C–N double-bond character, and is shifted to higher frequencies (1 493 and 1 490 cm^{-1}) for the phosphorus and arsenic compounds, respectively. The increase in C–N double-bond character is due to release of the electrons on the nitrogen atom of the NR_2 groups, resulting in high electron density on the sulphur atoms *via* the π system.[21] Nonetheless, the presence of a strong single band for the complex in this region is an argument used to support bidentate behaviour of the ligand. On the other hand, the main stretching frequency of the C–S bonds appeared as a doublet at 1 085 and 1 070 cm^{-1} for the phosphorus, 1 080 and 1 070 cm^{-1} for the arsenic compound. These two bands, with separations of less than 20 cm^{-1}, suggest that the diethyldithiocarbamates are anisobidentate, *i.e.* the two sulphur atoms are involved in bonds with different distances.[22,23] *X*-Ray structure determinations of these compounds have confirmed this conclusion.[24,25]

Although the molecular parent ion for the arsenic compound has been reported,[26] this peak did not appear in our mass spectrum. The general profiles of the fragments derived from the diethyldithiocarbamate radical are the same for both compounds: *m/z* 148 (Et_2NCS_2), 116 (Et_2NCS), 88 (EtHNCS), 56 (EtNHC), 76 (CS_2), 72 (Et_2N), 60 (H_2NCS), and 29 (Et). For the arsenic compound the first fragment derived from the molecular parent ion at *m/z* 271 [$As(S_2CNEt_2)_2$] is probably due to cleavage of the two arsenic–sulphur bonds with loss of the diethyldithiocarbamate radical.[27] The ease of this fragmentation is attributed to the existence of the inert lone pair of electrons on the arsenic atom.[21] This peak is followed by ones at *m/z* 254 ($SAsS_2CNEt$) and 223 (AsS_2CNEt_2), while for the phosphorus compound only the peak at *m/z* 179 (PS_2CNEt_2) was observed.

The enthalpies of formation of the phosphorus and arsenic chelates can be expressed in terms of the general reaction (1),

$$ECl_3(l) + 3[NH_2Et_2][S_2CNEt_2](c) \longrightarrow E(S_2CNEt_2)_3(c) + 3[NH_2Et_2]Cl(c);\ \Delta_rH^\circ_m \quad (1)$$

where E represents As or P. The determination of the enthalpies of dissolution of the reactants and products in acetone, while maintaining strict control of the stoicheiometries in each step of the reactions, leads to the molar enthalpy of the reaction ($\Delta_rH^\circ_m$). In this process, the final solution obtained by dissolution of reactants has the same composition as that upon dissolution of the products.[8,17] The general sequence of measurements in the calorimetric vessel is given in Table 1. The final solution A_2 is thermodynamically equivalent to A_4, and the same applies to solutions B_2 and B_4. By applying the first law of thermodynamics to the values listed in Table 1, $\Delta_rH^\circ_m = \Delta_1H^\circ_m + \Delta_2H^\circ_m - \Delta_3H^\circ_m - \Delta_4H^\circ_m = -317.28 \pm 2.22$ and $\Delta_rH^\circ_m = \Delta_5H^\circ_m + \Delta_6H^\circ_m - \Delta_7H^\circ_m - \Delta_8H^\circ_m = -132.16 \pm 0.44$ kJ mol^{-1} for the phosphorus and arsenic compounds, respectively. It is worth mentioning that the sequence of dissolution steps used for the phosphorus compounds was chosen to obtain a largely exothermic value for the dissolution of phosphorus chloride.

The standard molar enthalpies of formation of the crystalline chelates in Table 2 were obtained by means of expression (2)

$$\Delta_fH^\circ_m[E(S_2CNEt_2)_3,c] = \Delta_rH^\circ_m - 3\Delta_fH^\circ_m([NH_2Et_2]Cl,c) + \Delta_fH^\circ_m(ECl_3,l) + 3\Delta_fH^\circ_m([NH_2Et_2][S_2CNEt_2],c) \quad (2)$$

together with the standard molar enthalpies of formation listed in Table 3.

Thermochemical data for the compounds in the gas phase are necessary for determination of the bond enthalpies. However, all attempts to sublime these compounds were unsuccessful. Therefore, this parameter was determined by means of differential scanning calorimetry (d.s.c.). The thermogram showed sharp peaks of fusion at 404 and 416 K for the phosphorus and arsenic compounds, respectively, from which were calculated the enthalpies of fusion. The standard enthalpies of vaporization at 503 and 539 K, respectively, were estimated by the

Table 1. Standard molar enthalpies of solution and reaction in acetone at 298.15 K

i	Reactant	Solvent	Solution	No. of expts.	$\Delta_iH^\circ_m$/kJ mol^{-1}
1	$[NH_2Et_2][S_2CNEt_2](c)$	Acetone	A_1	5	48.45 ± 0.55
2	$PCl_3(l)$	A_1	A_2	5	−304.10 ± 2.09
3	$P(S_2CNEt_2)_3(c)$	Acetone	A_3	5	42.07 ± 0.51
4	$[NH_2Et_2]Cl(c)$	A_3	A_4	5	19.56 ± 0.10
5	$AsCl_3(l)$	Acetone	B_1	6	−7.46 ± 0.02
6	$[NH_2Et_2][S_2CNEt_2](c)$	B_1	B_2	4	−46.46 ± 0.26
7	$As(S_2CNEt_2)_3(c)$	Acetone	B_3	4	55.39 ± 0.32
8	$[NH_2Et_2]Cl(c)$	B_2	B_4	5	22.84 ± 0.16

Table 2. Standard molar enthalpies (kJ mol^{-1}), heat capacities (kJ K^{-1} mol^{-1}), and homolytic and heterolytic parameters (kJ mol^{-1})

	$P(S_2CNEt_2)_3$	$As(S_2CNEt_2)_3$
$\Delta_f H^{\ominus}_m$	-304.5 ± 7.6	-104.5 ± 7.6
$\Delta_s^l H^{\ominus}_m$	39.67 ± 1.15	34.10 ± 1.00
$\Delta_l^g H^{\ominus}_m$	42.48 ± 1.79	56.40 ± 3.02
$C_p(s)$	0.732 ± 0.022	0.548 ± 0.013
$C_p(l)$	0.959 ± 0.007	0.850 ± 0.047
$C_p(g)$	0.544 ± 0.190	0.561 ± 0.211
$\Delta_s^g H^{\ominus}_m$	143 ± 2	124 ± 3
$\Delta_{ho} H^{\ominus}_m$	$1\,123.8 \pm 21.0$	930.5 ± 21.2
$\Delta_{he} H^{\ominus}_m$	$6\,368.1 \pm 21.0$	$5\,827.9 \pm 21.1$

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

	$\Delta_f H^{\ominus}_m$	Ref.
$PCl_3(l)$	-319.7 ± 0.3	*
$AsCl_3(l)$	-305.0 ± 2.2	*
P(g)	314.6 ± 0.2	*
As(g)	302.5 ± 0.2	*
$P^{3+}(g)$	$6\,160.1 \pm 0.1$	*
$As^{3+}(g)$	$5\,801.1 \pm 0.1$	*
$[NH_2Et_2][S_2CNEt_2](c)$	-248.9 ± 2.1	8
$[NH_2Et_2]Cl(c)$	-359.73 ± 1.22	8
$HS_2CNEt_2(g)$	49.0 ± 4.2	8
$S_2CNEt_2^{\bullet}(g)$	215.9 ± 6.5	8
$S_2CNEt_2^{-}(g)$	15.5 ± 6.5	8

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Giacolone,[28] Riedel–Planck–Miller,[28] and Watson[29] methods. The results obtained by these methods were consistent and the mean value obtained for each compound is listed in Table 2. From the d.s.c. thermograms the heat capacities of both compounds in the solid state, at 390—400 K, or in the liquid state, at 470—480 and 425—435 K, respectively, were determined (Table 2). The gas-phase heat capacities were estimated by the method of generalised vibrational assignment,[29] which resulted in the expression: $C_p(g) = -6.43 \times 10^{-2} + 1.89 \times 10^{-3}\,T - 8.84 \times 10^{-7}T^2$. Application of all these auxiliary data to expression (3) resulted in the standard enthalpies of sublimation (Table 2).

$$\Delta_s^g H^{\ominus}_m(298) = \int_{298}^{T_{fus}} C_p(c)\mathrm{d}T + \Delta_s^l H^{\ominus}_m(T_{fus}) + \int_{T_{fus}}^{T_{vap}} C_p(l)\mathrm{d}T + \Delta_l^g H^{\ominus}_m(T_{vap}) - \int_{298}^{T_{vap}} C_p(g)\mathrm{d}T \quad (3)$$

The homolytic and heterolytic parameters for the element–ligand bond can be derived from the enthalpies of formation of both compounds in the gas phase.[8] The vibrational results clearly demonstrate that all the diethyldithiocarbamate groups are bound to the elements in a bidentate manner *via* sulphur. Therefore, the homolytic parameter is defined by expression (4).

$$E(g) + 3S_2CNEt_2^{\bullet}(g) \longrightarrow E(S_2CNEt_2)_3(g);\ \Delta_{ho}H \quad (4)$$

This value is related to the enthalpy of formation of the compound from the element and radical in their lowest energy states. Neglecting the reorganisation energy associated with the ligand upon complexation and assuming the equivalence of all element–sulphur bonds, then $\Delta_{ho}H = 6\bar{D}(E\text{–}S)$, where D is the mean bond enthalpy. At this point, it is worth remembering that for this bidentate ligand the two sulphur–central atom bonds are not exactly equivalent.[24,25]

The parameter $\Delta_{he}H$ is related to the enthalpy of formation of the gaseous chelate from the reactant ions in their lowest energy states. Expression (5) enabled the calculation of this parameter,

$$E^{3+}(g) + 3S_2CNEt_2^{-}(g) \longrightarrow E(S_2CNEt_2)_3(g);\ \Delta_{he}H \quad (5)$$

$\Delta_{he}H = -6\bar{D}'(E\text{–}S)$. With the auxiliary data listed in Table 3, the mean bond enthalpies $\bar{D}(E\text{–}S)$ and $\bar{D}'(E\text{–}S)$ for the phosphorus–sulphur bonds, 187.3 ± 3.5 and $1\,061.3 \pm 3.5$ kJ mol^{-1}, respectively, were obtained. The corresponding values for the arsenic–sulphur bond are 155.1 ± 3.5 and 971.8 ± 3.5 kJ mol^{-1}.

The available thermochemical data for sulphur bond enthalpy are limited to the adducts of thiourea,[30] some organometallic complexes[31] and carbamate complexes,[6,7] such as the dithiocarbamates of zinc and cadmium[5] and diethyldithiocarbamates of nickel, copper, and zinc.[8] The three last complexes showed a decrease in $\bar{D}(M\text{–}S)$ with increasing mean metal–sulphur bond distance. However, the opposite behaviour was observed for $\bar{D}'(M\text{–}S)$.

The thermochemical results decrease from phosphorus to arsenic with increasing mean bond distance, which was derived from crystallographic studies to be 257 and 260 pm for phosphorus–sulphur[24] and arsenic–sulphur,[25] respectively. Nevertheless, a small difference in distance causes a large disparity in the enthalpies, for example, in $\bar{D}(E\text{–}S)$. Of course, the higher enthalpy of the phosphorus–sulphur bond must be associated with a more effective bond.

Although the participation of *d* orbitals in bonds involving non-metals is open to debate,[32] arguments in favour of the overlap of the *d* orbitals of the E and sulphur atoms with the participation of a π bond have been used to explain the differences in the mean enthalpies of E–S bonds.[33] For example, the higher $\bar{D}(P\text{–}S)$ value suggests a strengthening of the bond between these atoms *via* a π bond, as a consequence of the better overlap of the *d* orbitals. In the case of the larger arsenic atom with more diffuse *d* orbitals the poorer overlap of the orbitals would result in a lower value for $\bar{D}(As\text{–}S)$. The same sort of argument is consistent with the hard and soft acids and bases principle. Thus, the effectiveness of the π bonding with arsenic can be explained by its lower ability to accept electrons from the soft sulphur atoms of the ligands, since hardness increases from phosphorus to arsenic.[34]

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