Journal of Thermal Analysis and Calorimetry, Vol. 67 (2002) 413–417

THERMOCHEMICAL PROPERTIES OF PALLADIUM(II) CHELATES INVOLVING DIALKYLDITHIOCARBAMATES

J. R. Botelho[1*], *A. G. Souza*[1], *L. M. Nunes*[1], *A. P. Chagas*[2], *I. M. Garcia dos Santos*[1], *M. M. da Conceição*[1] *and P. O. Dunstan*[2]

[1]Departamento de Química, CCEN, Universidade Federal da Paraíba, 58059-900, João Pessoa, Paraíba, Brazil
[2]Instituto de Química, Universidade Estadual de Campinas, 13083-970, Campinas, São Paulo, Brazil

Abstract

The standard molar enthalpies of formation of crystalline dialkyldithiocarbamates chelates, $[Pd(S_2CNR_2)_2]$, with $R=C_2H_5$, n-C_3H_7, n-C_4H_9 and i-C_4H_9, were determined through reaction-solution calorimetry in acetone, at 298.15 K. From the standard molar enthalpies of formation of the gaseous chelates, the homolytic (172.4±3.8, 182.5±3.2, 150.9±3.1 and 162.6±3.1 kJ mol^{-1}) and heterolytic (745.0±3.8, 803.7±3.3, 834.3±3.1 and 735.2±3.0 kJ mol^{-1}) mean palladium-sulphur bond-dissociation enthalpies were calculated.

Keywords: calorimetry, dialkyldithiocarbamates, enthalpies, palladium

Introduction

The thermochemical data found in literature concerning dithiocarbamates are essentially originating from application of several techniques such as: thermogravimetry, differential thermal analysis, differential scanning calorimetry, chromatography in gaseous phase, mass spectrometry and, in minor extension from solution calorimetry and thermometric titration [1–8].

This publication focuses on the thermochemical data for Pd(II) chelates of dialkyldithiocarbamates. These results are useful for helping to understand the effect of the length of the alkyl chain bonded to the nitrogen atom of the ligand, over the thermochemical parameters of the chelates.

Experimental

The salts dialkyl ammonium chloride, R_2NH_2Cl, and dialkylammonium dialkyldithiocarbamate, $R_2NH_2S_2CNR_2$, were synthesized with $R=C_2H_5$, n-C_3H_7, n-C_4H_9 and

---

[*] Author for correspondence: E-mail: regisbotelho@uol.com.br

1418–2874/2002/ $ 5.00

Akadémiai Kiadó, Budapest
Kluwer Academic Publishers, Dordrecht

i-C_4H_9. Their chemical analysis and melting points were in complete agreement with their postulated formulation and reported melting points [5–8]. The palladium(II) dialkyldithiocarbamates complexes, $[Pd(S_2CNR_2)_2]$, with R=C_2H_5, n-C_3H_7, n-C_4H_9, and i-C_4H_9 were synthesized from the direct reaction of $PdCl_2$ with the corresponding amine and carbon disulphide using 1,2-dichloroethane as the solvent.

The microanalysis (C, H, N) of the chelates were carried out using a Perkin Elmer elemental analyser. Infrared spectra were recorded with the compounds in KBr pellets on a BOMEM, model MB-102 spectrophotometer. The melting point temperatures for all compounds were determined by means of a MICROQUÍMICA, model MQAPF-301 apparatus. Thermogravimetric curves were obtained using a Shimadzu model TGA-50 thermobalance, at a heating rate of 10°C min^{-1} in a dynamic atmosphere of dry nitrogen flux of 50 mL min^{-1} and the mass spectra of the ligands and their Pd(II) chelates, were recorded on a Hewlett–Packard model 5988A spectrometer with an ionization energy of 70 eV, at 523 K.

All solution calorimetric determinations were carried out in LKB 8700-1 isoperibolic precision calorimeter system as described before [9].

The melting enthalpies and the heat capacities of the chelates were determined in a Shimadzu model DSC-50 differential scanning calorimeter, at a heating rate of 5 K min^{-1} purged with dry nitrogen [9, 10].

Results and discussion

The CHN elemental analysis of the complexes, $[Pd(S_2CNR_2)_2]$, with R=C_2H_5, n-C_3H_7, n-C_4H_9, and i-C_4H_9, are in good agreement with the expected values for the postulated formulation of these compounds. The melting points observed for them are consistent with their high purities. The mode of coordination of the dialkyldithiocarbamates and the defined melting points suggest the existence of very stable compounds. However, on cooling the molten samples and heating them again, the previous melting-point intervals were not reproduced.

The band attributed to νCN in the IR spectra of the ligands, splits into two after coordination, one of which is shifted to higher frequencies relative to the uncoordinated ligands. For all complexes this band frequency is higher than that of the respective ligand. On the other hand, a decrease in the band attributed to CS is observed in the chelates relative to the uncoordinated ligands, and a new band at 1000 cm^{-1} appears, indicating that the ligands are bonded in a bidentate way to the metallic ion [11]. The mass spectra of the complexes revealed the presence of the parent ions with the following stability order: $Pd(S_2CNPr^n_2)_2 > Pd(S_2CNBu^n_2)_2 > Pd(S_2CNEt_2)_2 > Pd(S_2CNBu^i_2)_2$).

The standard molar enthalpies of reaction, $\Delta_r H^o_m$, were obtained at 298.15 K, from the reaction-solution enthalpies, $\Delta_i H^o_m$, of each reagent and product dissolved sequentially in 1,2-dichloroethane (Table 1), where a strict control of stoichiometry was maintained, for the following general reaction [5–8]:

$$PdCl_2(cr)+2NH_2R_2S_2CNR_2(cr) \rightarrow Pd(S_2CNR_2)_2(cr)+2NH_2R_2Cl(cr);\Delta_r H^o_m \quad (1)$$

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

Reactant	Solvent	Solution	$\Delta_i H^o_m$
$2Et_2NH_2S_2CNEt_r$(*cr*)	1,2-dichloroethane	A_1	67.66±1.23
$PdCl_2$(*cr*)	A_1	A_2	34.79±2.18
$Pd(S_2CNEt_2)_2$(*cr*)	1,2-dichloroethane	A_3	12.04±0.46
$2Et_2NH_2Cl$(*cr*)	A_3	A_4	1.99±0.01
$2Pr^n_2NH_2S_2CNPr^n_2$(*cr*)	1,2-dichloroethane	B_1	42.81±0.95
$PdCl_2$(*cr*)	B_1	B_2	21.73±1.97
$Pd(S_2CNPr^n_2)_2$(*cr*)	1,2-dichloroethane	B_3	41.03±1.86
2Pr*n*2NH$_2$Cl(*cr*)	B_2	B_4	18.01±1.05
$2Bu^n_2NH_2S_2CNBu^n_2$(*cr*)	1,2-dichloroethane	D_1	34.54±0.42
$PdCl_2$(*cr*)	D_1	D_2	18.34±2.01
$Pd(S_2CNBu^n_2)_2$(*cr*)	1,2-dichloroethane	D_3	46.20±0.68
$2Bu^n_2NH_2Cl$(*cr*)	D_3	D_4	27.24±0.51
$2Bu^i_2NH_2S_2CNBu^i_2$(*cr*)	1,2-dichloroethane	E_1	36.76±0.77
$PdCl_2$(*cr*)	E_1	E_2	19.98±1.98
$Pd(S_2CNBu^i_2)_2$(*cr*)	1,2-dichloroethane	E_3	21.58±1.08
$2Bu^i_2NH_2Cl$(*cr*)	E_3	E_4	28.50±0.58

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

Parameters	$Pd(S_2CNEt_2)_2$	$Pd(S_2CNPr^n_2)_2$	$Pd(S_2CNBu^n_2)_2$	$Pd(S_2CNBu^i_2)_2$
$\Delta_r H^o_m$	88.42±2.54	5.50±3.06	–20.56±2.22	6.66±2.45
$\Delta_f H^o_m(cr)$	110.78±6.42	–120.60±5.44	–237.72±5.03	–197.50±4.93
$\Delta^l_{cr} H^o_m$	36.68±3.52	30.32±0.88	27.18±3.52	25.49± 3.96
$\Delta^g_l H^o_m$	58.96±2.64	63.79±3.96	64.41±0.44	64.08±3.52
T_{fus}	503	416	375	465
T_{vap}	582	594	587	597
$C_{p,m}(cr)$	0.271	0.573	0.511	0.799
$C_{p,m}(l)$	0.124	0.649	0.700	0.991
$C_{p,m}(g)$	0.533	0.692	0.833	0.848
$\Delta^g_{cr} H^o_m$	9.65±4.40	72.41±4.06	38.44±3.55	100.13±5.30
$\Delta_f H^o_m(g)$	120.43±7.60	–48.19±6.49	–139.30±7.58	–97.37±5.03
$\Delta_{ho} H^o_m$	–689.57±15.08	–729.99±12.98	–603.70±12.42	–650.57±12.13
$\Delta_{he} H^o_m$	–2979.97±15.16	–3214.79±13.07	–3337.30±12.51	–2940.97±12.22
$\langle D \rangle$(Pd–S)	172.4±3.8	182.5±3.2	150.9±3.1	162.6±3.0
$\langle D' \rangle$(Pd–S)	745.0±3.8	803.7±3.3	834.3±3.1	735.2±3.0

The standard molar enthalpy for each reaction was calculated from these tabulated values by applying a convenient thermochemical cycle. The individual enthalpies values are listed in Table 2.

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

Species	$\Delta_f H^o_m$	Ref.
$PdCl_2(cr)$	–198.70±3.08	[12]
$Et_2NH_2S_2CNEt_2(cr)$	–249.2±2.2	[13]
$Et_2NH_2Cl(cr)$	–359.73±1.22	[14]
$Pr^n_2NH_2S_2CNPr^n_2(cr)$	–353.20±1.30	[13]
$Pr^n_2NH_2Cl(cr)$	–389.50±1.00	[8]
$Bu^n_2NH_2S_2CNBu^n_2(cr)$	–461.3±1.6	[13]
$Bu^n_2NH_2Cl(cr)$	–452.44±0.39	[8]
$Bu^i_2NH_2S_2CNBu^i_2(cr)$	–463.8±1.4	[13]
$Bu^i_rNH_2Cl(cr)$	–461.07±0.50	[8]
$Pd(g)$	378.20±0.88	[12]
$Pd^{2+}(g)$	3069.40±1.76	[12]
$Et_2NCS^{\cdot}_2(g)$	215.9±6.5	[9]
$Et_2NCS^-_2(g)$	15.5±6.5	[9]
$Pr^n_2NCS^{\cdot}_2(g)$	151.8±5.6	[6]
$Pr^n_2NCS^-_2(g)$	48.6±5.6	[6]
$Bu^n_2NCS^{\cdot}_2(g)$	117.9±5.5	[10]
$Bu^n_2NCS^-_2(g)$	82.5±5.5	[10]
$Bu^i_2NCS^{\cdot}_2(g)$	87.5±7.6	[5]
$Bu^i_2NCS^-_2(g)$	112.9±7.6	[5]

The standard molar enthalpies of formation of the crystalline chelates shown in Table 2, were determined from: a) the values of $\Delta_r H^o_m$, b) the standard molar enthalpies of formation of the palladium chloride [12], ligands [13] and dialkyl ammonium chlorides [14], c) by using expression (2), d) the auxiliary data listed in Table 3.

$$\Delta_f H^o_m[\mathrm{ln(S_2CNR_2)_3}](cr)=\Delta_r H^o_m-3\Delta_f H^o_m(\mathrm{NH_2R_2Cl})(cr)+\Delta_f H^o_m(\mathrm{lnCl_3})(cr)$$
$$+3\Delta_f H^o_m(\mathrm{NH_2R_2S_2CNR_2})(cr) \qquad (2)$$

The standard molar enthalpies of sublimation, $\Delta^g_{cr}H^o_m$, were determined by means of differential scanning calorimetry and estimation methods [5–8,15].

The molar standard enthalpies of vaporization were determined through estimative methods [8]. The molar standard enthalpies of melting and heat capacities for the solid and liquid phases of the chelates were determined by DSC technique. However, for the gas phase these quantities were estimated [8]. A complete series of these values obtained are listed in Table 2, together with the standard molar enthalpies of sublimation. These values were calculated by applying all these data in the expression (3) and consequently the standard molar enthalpies of formation in the gas phase, listed in Table 2, were calculated.

$$\Delta_{\mathrm{cr}}^{\mathrm{g}} H_{\mathrm{m}}^{\mathrm{o}} = \int_{298.15\ \mathrm{K}}^{\mathrm{T_{fus}}} C_{\mathrm{p}}(cr)\mathrm{d}T + \Delta_{\mathrm{cr}}^{\mathrm{l}} H_{\mathrm{m}}^{\mathrm{o}} + \int_{\mathrm{T_{fus}}}^{\mathrm{T_{vap}}} C_{\mathrm{p}}(l)\mathrm{d}T + \Delta_{\mathrm{l}}^{\mathrm{g}} H_{\mathrm{m}}^{\mathrm{o}} + \int_{\mathrm{T_{vap}}}^{298.15\ \mathrm{K}} C_{\mathrm{p}}(g)\mathrm{d}T \qquad (3)$$

The auxiliary data listed in Table 3 enable the calculation of the mean enthalpies of palladium–sulphur bonds [5–8, 10] for homolytic, $\langle D\rangle(\mathrm{Pd}-S)=\Delta_{\mathrm{ho}}H_{\mathrm{m}}^{\mathrm{o}}/4$ and heterolytic, $\langle D'\rangle(\mathrm{Pd}-S)=\Delta_{\mathrm{he}}H_{\mathrm{m}}^{\mathrm{o}}/4$ processes. These calculated values are listed in Table 2.

Conclusions

The results presented in Table 2 show that $\langle D\rangle(\mathrm{Pd}-S)$ and $\langle D'\rangle(\mathrm{Pd}-S)$ values follow a different sequence as compared with the expected one. This behaviour demonstrates clearly that, in the case of alkyl substitution, the possible polar or steric effects related to it did not affect directly the interaction Pd–S as the final result did not indicate any clear dependence on either of these effects.

* * *

The authors thank CNPq Foundation (Brazil) for the scholarships and financial support for the accomplishment of this work.

References

1 M. A. Bernard and M. Borel, Bull. Soc. Chem. Fr., 9 (1969) 3064.
2 J. O. Hill and R. J. Magee, Rev. Inorg. Chem., 3 (1981) 141.
3 P. M. Burkinshaw and C. T. Mortimer, Coord. Chem. Rev., 48 (1983) 101.
4 C. Airoldi and A. P. Chagas, Coord. Chem. Rev., 119 (1992) 29.
5 A. G. Souza, F. Souza Neto, J. H. Souza, R. O. Macêdo, J. B. L. Oliveira and C. D. Pinheiro, J. Thermal Anal., 49 (1997) 679.
6 M. A. R. P. Carvalho, A. G. Souza and C. Airoldi, J. Chem. Soc., Dalton Trans., (1992) 1235.
7 A. G. Souza, C. D. Pinheiro, L. C. R. Santos and M. L. M. Melo, Thermochim. Acta, 231 (1994) 31.
8 L. P. M. Neves, A. G. Souza, J. B. L. Oliveira and C. Airoldi, Thermochim. Acta, 328 (1999) 217
9 S. C. Dias, M. G. A. Brasilino, C. D. Pinheiro and A. G. Souza, Thermochim. Acta, 241 (1994) 25.
10 C. Airoldi and A. G. Souza, J. Chem. Thermodyn., 21 (1989) 283.
11 F. Bonati and R. Ugo, J. Orgametal. Chem., 10 (1967) 257.
12 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, Suppl., 2 (1982) 11.
13 M. A. V. Ribeiro da Silva, A. M. V. Reis and G. Pilcher, J. Chem. Thermodyn., 19 (1987) 837.
14 A. G. Souza, C. D. Pinheiro and C. Airoldi, Polyhedron, 11 (1992) 371.
15 R. C. Reid and T. K. Sherwood, The Properties of Gases and Liquids, 2nd edn., McGraw–Hill, New York 1968.