Thermochimica Acta, 131 (1988) 103–106
Elsevier Science Publishers B V , Amsterdam – Printed in The Netherlands

ENTHALPY OF FORMATION OF *trans*-$PdCl_2(TeEt_2)_2$

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(Received 24 November 1987)

ABSTRACT

The enthalpy change of the reaction $(NH_4)_2PdCl_4(c) + 2Et_2Te(l)$ = *trans*-$PdCl_2(TeEt_2)_2(c) + 2NH_4Cl(c)$ has been determined calorimetrically as $\Delta H = (175\ 7 \pm 4\ 8)$ kJ mol^{-1} The values $\Delta H_f^{\ominus}$[*trans*-$PdCl_2(SEt_2)_2$,c] $= -(563\ 7 \pm 3\ 9)$ kJ mol^{-1}, $\Delta H_f^{\ominus}$[*trans*-$PdCl_2)(SeEt_2)_2$,c] $= -(529\ 2 \pm 9\ 5)$ kJ mol^{-1} and $\Delta H_f^{\ominus}$[*trans*-$PdCl_2)TeEt_2)_2$,c] $= -(763\ 8 \pm 14\ 6)$ kJ mol^{-1} are reported The mean bond dissociation energies $\bar{D}$(Pd–Te) = $\bar{D}$(Pd–Se) = $\bar{D}$(Pd–S) = 200 ± 10 kJ mol^{-1} are calculated

INTRODUCTION

Previously [1], we have shown that the mean bond dissociation energies of the Pd–S and Pd–Se bonds in the complexes *trans*-$PdCl_2(SEt_2)_2$ and *trans*-$PdCl_2(SeEt_2)_2$ are very similar, the question arises whether the Pd–Te bond in *trans*-$PdCl_2(TeEt_2)_2$ is weaker or stronger than the Pd–S and Pd–Se bonds To attempt to answer this question the enthalpy of the following reaction has been determined

$$trans\text{-}PdCl_2(TeEt_2)_2(g) = PdCl_2(g) + 2Et_2Te(g)$$

This has been achieved by measurement of the enthalpy changes $\Delta H(1)$ to $\Delta H(3)$ of reactions (1)–(3) The enthalpies of reactions (4) and (5) have been measured previously [1].

$$\begin{aligned}&[(NH_4)_2PdCl_4 + 760CH_3COCH_3 + 820H_2O] + (2+x)Et_2Te(l)\\&\quad = [2NH_4Cl + trans\text{-}PdCl_2(TeEt_2)_2 + xEt_2Te\\&\qquad + 760CH_3COCH_3 + 820H_2O] \qquad (1)\end{aligned}$$

$$\begin{aligned}&xEt_2Te(l) + [2NH_4Cl + trans\text{-}PdCl_2(TeEt_2)_2 + 760CH_3COCH_3 + 820H_2O]\\&\quad = [2NH_4Cl + trans\text{-}PdCl_2(TeEt_2)_2 + xEt_2Te\\&\qquad + 760CH_3COCH_3 + 820H_2O] \qquad (2)\end{aligned}$$

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$$\begin{aligned}&\textit{trans}\text{-}\mathrm{PdCl_2(TeEt_2)_2(c)} + [\mathrm{2NH_4Cl + 760CH_3COCH_3 + 820H_2O}]\\ &\quad = [\mathrm{2NH_4Cl} + \textit{trans}\text{-}\mathrm{PdCl_2(TeEt_2)_2 + 760CH_3COCH_3 + 820H_2O}]\end{aligned} \tag{3}$$

$$\begin{aligned}&\mathrm{NH_4Cl(c)} + [\mathrm{380CH_3COCH_3 + 410H_2O}]\\ &\quad = [\mathrm{NH_4Cl + 380CH_3COCH_3 + 410H_2O}]\end{aligned} \tag{4}$$

$$\begin{aligned}&\mathrm{(NH_4)_2PdCl_4(c)} + [\mathrm{760CH_3COCH_3 + 820H_2O}]\\ &\quad = [\mathrm{(NH_4)_2PdCl_4 + 760CH_3COCH_3 + 820H_2O}]\end{aligned} \tag{5}$$

EXPERIMENTAL

trans-$\mathrm{PdCl_2(TeEt_2)_2}$ was prepared by addition of $\mathrm{Et_2Te}$ (3 mol) to an aqueous solution of $\mathrm{(NH_4)_2PdCl_4}$ (1 mole) [2] and recrystallized from methanol, m p 371 K (literature value [3] 372 K), found C 17 7, H 3 53, Pd 19 41 (by precipitation as 2-thiophene *trans*-aldoxime complex), calc for $\mathrm{C_8H_{20}Cl_2Te_2Pd}$, C 17 5, H 3 67, Pd 19 39 mass% $\mathrm{(NH_4)_2PdCl_4}$ (Johnson Matthey) found Pd 37 41 (by precipitation as dimethylglyoxime complex), calc for $\mathrm{(NH_4)_2PdCl_4}$, Pd 37 43 mass% $\mathrm{Et_2Te}$ (Strem Chemicals) was distilled under nitrogen, b p 409–410 K, 745 torr Acetone (Hopkin and Williams) was purified by use of potassium permanganate [4]

Enthalpies of reactions were measured by use of the LKB precision solution calorimeter 8700 equipped with the 25 ml vessel Reactions were initiated at 298 15 K The following values were obtained $\Delta H(1) - x\,\Delta H(2) = -(119\ 9 \pm 4\ 1)$ kJ mol^{-1}, $\Delta H(2) = +(9\ 4 \pm 0.7)$ kJ mol^{-1}, and $\Delta H(3) = +(50\ 5 \pm 0\ 5)$ kJ mol^{-1} The enthalpies of reactions (4) and (5) have been given previously [1] as $\Delta H(4) = +(8\ 99 \pm 0\ 05)$ kJ mol^{-1} and $\Delta H(5) = +(12\ 7 \pm 0\ 1)$ kJ mol^{-1}

DISCUSSION

The enthalpy change $\Delta H(6)$ of reaction (6) may be calculated from the relationship $\Delta H(6) = [\Delta H(1) - x\Delta H(2) - \Delta H(3) - 2\Delta H(4) + \Delta H(5)] = -(175\ 7 \pm 4\ 8)$ kJ mol^{-1}

$$\mathrm{(NH_4)_2PdCl_4(c) + 2Et_2Te(l)} = \textit{trans}\text{-}\mathrm{PdCl_2(TeEt_2)_2(c) + 2NH_4Cl(c)} \tag{6}$$

$$\textit{trans}\text{-}\mathrm{PdCl_2(TeEt_2)_2(g) = PdCl_2(g) + 2Et_2Te(g)} \tag{7}$$

$$\textit{trans}\text{-}\mathrm{PdCl_2(SeEt_2)_2(g) = PdCl_2(g) + 2Et_2Se(g)} \tag{8}$$

$$\textit{trans}\text{-}\mathrm{PdCl_2(SEt_2)_2(g) = PdCl_2(g) + 2Et_2S(g)} \tag{9}$$

The enthalpy $\Delta H(7)$ of reaction (7) can be calculated by incorporating the values $\Delta H_f^\ominus[\mathrm{(NH_4)_2PdCl_4,c}] = -(841.0 \pm 1.7)$ kJ mol^{-1} [5], $\Delta H_f^\ominus(\mathrm{NH_4Cl,c}) = -(314\ 43 \pm 0\ 05)$ kJ mol^{-1} [6], $\Delta H_f^\ominus(\mathrm{PdCl_2,c}) =$

$-(163\ 2 \pm 10)$ kJ mol^{-1} [7], ΔH_{vap} $\text{Et}_2\text{Te} = +(41\ 8 \pm 2)$ kJ mol^{-1} [8] and the term $a = [\Delta H_{\text{sub}}\text{PdCl}_2 - \Delta H_{\text{sub}}\textit{trans}\text{-PdCl}_2(\text{TeEt}_2)_2]$ This last term is introduced because the enthalpies of sublimation of these compounds are not available The value of $\Delta H(7)$ may be compared with the enthalpies of reactions (8) and (9), which may be recalculated from previously published data [1], where $b = [\Delta H_{\text{sub}}\text{PdCl}_2 - \Delta H_{\text{sub}}\textit{trans}\text{-PdCl}_2(\text{SeEt}_2)_2]$ and $c = [\Delta H_{\text{sub}} - \Delta H_{\text{sub}}\textit{trans}\text{-PdCl}_2(\text{SEt}_2)_2]$

$$\Delta H(7) = +(308 \pm 20)\ \text{kJ mol}^{-1} + a$$

$$\Delta H(8) = +(251 \pm 20)\ \text{kJ mol}^{-1} + b$$

$$\Delta H(9) = +(233 \pm 15)\ \text{kJ mol}^{-1} + c$$

The uncertainties associated with these values are large, mainly because of the large uncertainty of ±10 kJ mol^{-1} associated with the enthalpy of formation of crystalline PdCl_2 When considering differences between the values of $\Delta H(7)$, $\Delta H(8)$ and $\Delta H(9)$, this source of uncertainty is removed

Skinner [9] has assessed the available evidence and concludes that the enthalpy of sublimation of PdCl_2 is larger than that for PtCl_2 (251 kJ mol^{-1}) by about 40 kJ mol^{-1}, and uses the value $\Delta H_{\text{sub}}(\text{PdCl}_2) = 290$ kJ mol^{-1} He also concludes that the enthalpies of sublimation of the complexes PdL_2Cl_2 may be higher than the corresponding PtL_2X_2 complexes by 10 kJ mol^{-1} Enthalpies of sublimation of a number of these platinum complexes have been measured and relationships between ΔH_{sub} and molecular weight of the compounds have been established [9] These relationships have been used [10] to predict the ΔH_{sub} values $\text{Pd(SEt}_2)\text{Cl}_2$, 126 kJ mol^{-1}, $\text{Pd(SeEt}_2)_2\text{Cl}_2$, 160 kJ mol^{-1}, and $\text{Pd(TeEt}_2)_2\text{Cl}_2$ 192 kJ mol^{-1} Incorporating these values leads to the following enthalpies of the dissociation reactions (7)–(9), $\Delta H(7) = 406 \pm 20$ kJ mol^{-1}, $\Delta H(8) = 381 \pm 20$ kJ mol^{-1} and $\Delta H(9) = 397 \pm 20$ kJ mol^{-1}, so that we write $\bar{D}(\text{Pd–Te}) = \bar{D}(\text{Pd–Se}) = \bar{D}(\text{Pd–S}) = 200 \pm 10$ kJ mol^{-1} The strengths of the palladium–tellurium, palladium–selenium and palladium–sulphur bonds are the same.

We take this opportunity of up-dating the previously published [1] enthalpies of formation $\Delta H_f^{\ominus}[\textit{trans}\text{-PdCl}_2(\text{SEt}_2)_2,\text{c}] = -(550\ 9 \pm 4\ 9)$ kJ mol^{-1} and $\Delta H_f^{\ominus}[\textit{trans}\text{-PdCl}_2(\text{SeEt}_2)_2,\text{c}] = -(516\ 7 \pm 10\ 4)$ kJ mol^{-1} In calculating these values an error was introduced by incorporating into the calculation the quantity $\Delta H(4) = +(8\ 99 \pm 0\ 5)$ kJ mol^{-1} rather than the correct quantity $2\Delta H(4) = +(17\ 98 \pm 0\ 10)$ kJ mol^{-1} In addition, the older value $\Delta H_f^{\ominus}[(\text{NH}_4)_2\text{PdCl}_4,\text{c}] = -(837\ 8 \pm 2\ 8)$ kJ mol^{-1} was used Taking the more recent value $\Delta H_f^{\ominus}[(\text{NH}_4)_2\text{PdCl}_4,\text{c}] = -(841 \pm 1\ 1)$ kJ mol^{-1} [5], together with the values $\Delta H_f^{\ominus}(\text{Et}_2\text{S,l}) = -(119\ 4 \pm 0\ 8)$ kJ mol^{-1} [11], $\Delta H_f^{\ominus}(\text{Et}_2\text{Se,l}) = -(96\ 4 \pm 3\ 4)$ kJ mol^{-1} [11], which have been recalculated by Pedley and Rylance, and the value $\Delta H_f^{\ominus}(\text{Et}_2\text{Te,l}) = -(188\ 0 \pm 4)$ kJ mol^{-1} [8], leads to the values $\Delta H_f^{\ominus}[\textit{trans}\text{-PdCl}_2(\text{SEt}_2)_2,\text{c}] = -(563\ 7 \pm 3\ 9)$

kJ mol^{-1}, $\Delta H_{\mathrm{f}}^{\ominus}[\textit{trans}\text{-}\mathrm{PdCl_2(SeEt_2)_2,c}] = -(529\ 2 \pm 9\ 5)$ kJ mol^{-1} and $\Delta H_{\mathrm{f}}^{\ominus}[\textit{trans}\text{-}\mathrm{PdCl_2(TeEt_2)_2,c}] = -(763\ 8 \pm 14\ 6)$ kJ mol^{-1}

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