

ENTHALPY OF FORMATION OF *trans*-PdCl₂(TeEt₂)₂

A EVANS and C T MORTIMER

Department of Chemistry, The University of Keele, Keele, Staffordshire ST5 5BG (Gt Britain)

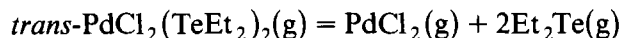
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ABSTRACT

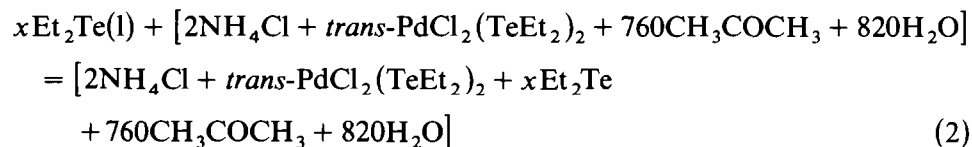
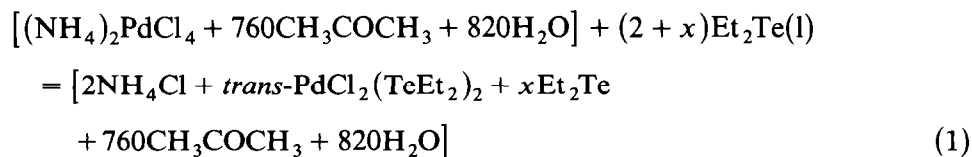
The enthalpy change of the reaction $(\text{NH}_4)_2\text{PdCl}_4(\text{c}) + 2\text{Et}_2\text{Te}(\text{l}) = \text{trans-PdCl}_2(\text{TeEt}_2)_2(\text{c}) + 2\text{NH}_4\text{Cl}(\text{c})$ has been determined calorimetrically as $\Delta H = (175.7 \pm 4.8) \text{ kJ mol}^{-1}$. The values $\Delta H_f^\ominus[\text{trans-PdCl}_2(\text{SEt}_2)_2, \text{c}] = -(563.7 \pm 3.9) \text{ kJ mol}^{-1}$, $\Delta H_f^\ominus[\text{trans-PdCl}_2(\text{SeEt}_2)_2, \text{c}] = -(529.2 \pm 9.5) \text{ kJ mol}^{-1}$ and $\Delta H_f^\ominus[\text{trans-PdCl}_2(\text{TeEt}_2)_2, \text{c}] = -(763.8 \pm 14.6) \text{ kJ mol}^{-1}$ are reported. The mean bond dissociation energies $\bar{D}(\text{Pd}-\text{Te}) = \bar{D}(\text{Pd}-\text{Se}) = \bar{D}(\text{Pd}-\text{S}) = 200 \pm 10 \text{ kJ mol}^{-1}$ are calculated.

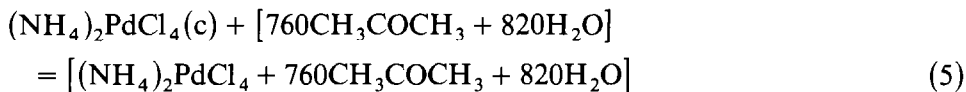
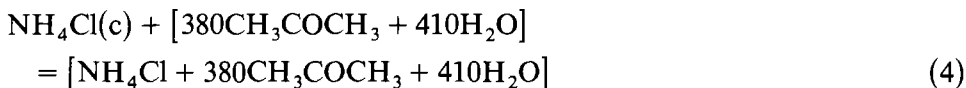
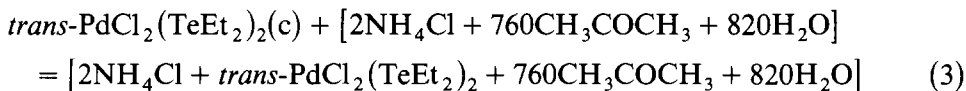
INTRODUCTION

Previously [1], we have shown that the mean bond dissociation energies of the Pd–S and Pd–Se bonds in the complexes *trans*-PdCl₂(SEt₂)₂ and *trans*-PdCl₂(SeEt₂)₂ are very similar, the question arises whether the Pd–Te bond in *trans*-PdCl₂(TeEt₂)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



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].





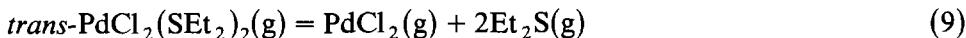
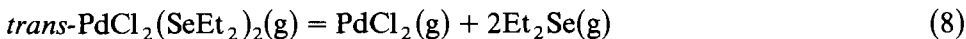
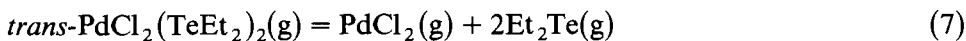
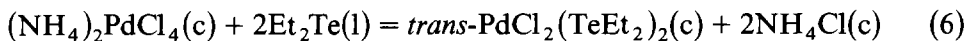
EXPERIMENTAL

trans-PdCl₂(TeEt₂)₂ was prepared by addition of Et₂Te (3 mol) to an aqueous solution of (NH₄)₂PdCl₄ (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 C₈H₂₀Cl₂Te₂Pd, C 17.5, H 3.67, Pd 19.39 mass% (NH₄)₂PdCl₄ (Johnson Matthey) found Pd 37.41 (by precipitation as dimethylglyoxime complex), calc for (NH₄)₂PdCl₄, Pd 37.43 mass% Et₂Te (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 $\Delta H(1) - x \Delta H(2) = -(119.9 \pm 4.1) \text{ kJ mol}^{-1}$, $\Delta H(2) = +(9.4 \pm 0.7) \text{ kJ mol}^{-1}$, and $\Delta H(3) = +(50.5 \pm 0.5) \text{ kJ mol}^{-1}$. The enthalpies of reactions (4) and (5) have been given previously [1] as $\Delta H(4) = +(8.99 \pm 0.05) \text{ kJ mol}^{-1}$ and $\Delta H(5) = +(12.7 \pm 0.1) \text{ kJ mol}^{-1}$.

DISCUSSION

The enthalpy change $\Delta H(6)$ of reaction (6) may be calculated from the relationship $\Delta H(6) = [\Delta H(1) - x\Delta H(2) - \Delta H(3) - 2\Delta H(4) + \Delta H(5)] = -(175.7 \pm 4.8) \text{ kJ mol}^{-1}$



The enthalpy $\Delta H(7)$ of reaction (7) can be calculated by incorporating the values $\Delta H_f^\ominus[(\text{NH}_4)_2\text{PdCl}_4, \text{c}] = -(841.0 \pm 1.7) \text{ kJ mol}^{-1}$ [5], $\Delta H_f^\ominus(\text{NH}_4\text{Cl}, \text{c}) = -(314.43 \pm 0.05) \text{ kJ mol}^{-1}$ [6], $\Delta H_f^\ominus(\text{PdCl}_2, \text{c}) =$

$-(163.2 \pm 10) \text{ kJ mol}^{-1}$ [7], $\Delta H_{\text{vap}} \text{Et}_2\text{Te} = +(41.8 \pm 2) \text{ kJ mol}^{-1}$ [8] and the term $a = [\Delta H_{\text{sub}} \text{PdCl}_2 - \Delta H_{\text{sub}} \text{trans-PdCl}_2(\text{TeEt}_2)_2]$. 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 $b = [\Delta H_{\text{sub}} \text{PdCl}_2 - \Delta H_{\text{sub}} \text{trans-PdCl}_2(\text{SeEt}_2)_2]$ and $c = [\Delta H_{\text{sub}} - \Delta H_{\text{sub}} \text{trans-PdCl}_2(\text{SEt}_2)_2]$

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

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

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

The uncertainties associated with these values are large, mainly because of the large uncertainty of $\pm 10 \text{ kJ mol}^{-1}$ 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 $\Delta H_{\text{sub}}(\text{PdCl}_2) = 290 \text{ kJ mol}^{-1}$. 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 $\text{Pd}(\text{SEt}_2)\text{Cl}_2$, 126 kJ mol^{-1} , $\text{Pd}(\text{SeEt}_2)_2\text{Cl}_2$, 160 kJ mol^{-1} , and $\text{Pd}(\text{TeEt}_2)_2\text{Cl}_2$, 192 kJ mol^{-1} . Incorporating these values leads to the following enthalpies of the dissociation reactions (7)–(9), $\Delta H(7) = 406 \pm 20 \text{ kJ mol}^{-1}$, $\Delta H(8) = 381 \pm 20 \text{ kJ mol}^{-1}$ and $\Delta H(9) = 397 \pm 20 \text{ kJ mol}^{-1}$, so that we write $\bar{D}(\text{Pd}-\text{Te}) = \bar{D}(\text{Pd}-\text{Se}) = \bar{D}(\text{Pd}-\text{S}) = 200 \pm 10 \text{ kJ mol}^{-1}$. 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 $\Delta H_f^\ominus[\text{trans-PdCl}_2(\text{SEt}_2)_2, \text{c}] = -(550.9 \pm 4.9) \text{ kJ mol}^{-1}$ and $\Delta H_f^\ominus[\text{trans-PdCl}_2(\text{SeEt}_2)_2, \text{c}] = -(516.7 \pm 10.4) \text{ kJ mol}^{-1}$. In calculating these values an error was introduced by incorporating into the calculation the quantity $\Delta H(4) = +(8.99 \pm 0.5) \text{ kJ mol}^{-1}$ rather than the correct quantity $2\Delta H(4) = +(17.98 \pm 0.10) \text{ kJ mol}^{-1}$. In addition, the older value $\Delta H_f^\ominus[(\text{NH}_4)_2\text{PdCl}_4, \text{c}] = -(837.8 \pm 2.8) \text{ kJ mol}^{-1}$ was used. Taking the more recent value $\Delta H_f^\ominus[(\text{NH}_4)_2\text{PdCl}_4, \text{c}] = -(841 \pm 1.1) \text{ kJ mol}^{-1}$ [5], together with the values $\Delta H_f^\ominus(\text{Et}_2\text{S}, \text{l}) = -(119.4 \pm 0.8) \text{ kJ mol}^{-1}$ [11], $\Delta H_f^\ominus(\text{Et}_2\text{Se}, \text{l}) = -(96.4 \pm 3.4) \text{ kJ mol}^{-1}$ [11], which have been recalculated by Pedley and Rylance, and the value $\Delta H_f^\ominus(\text{Et}_2\text{Te}, \text{l}) = -(188.0 \pm 4) \text{ kJ mol}^{-1}$ [8], leads to the values $\Delta H_f^\ominus[\text{trans-PdCl}_2(\text{SEt}_2)_2, \text{c}] = -(563.7 \pm 3.9)$

kJ mol^{-1} , $\Delta H_f^\ominus[\textit{trans}\text{-PdCl}_2(\text{SeEt}_2)_2, \text{c}] = -(529.2 \pm 9.5) \text{ kJ mol}^{-1}$ and $\Delta H_f^\ominus[\textit{trans}\text{-PdCl}_2(\text{TeEt}_2)_2, \text{c}] = -(763.8 \pm 14.6) \text{ kJ mol}^{-1}$

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