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ENTHALPIES OF FORMATION OF M(PENTANEDIONATO)$_2$ COMPLEXES (M = Ni AND Pd)

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ABSTRACT

Enthalpies of formation, ΔH_f^0, of the crystalline metal complexes M(pentanedionato)$_2$ have been determined by solution calorimetry as M = Ni, −861.0 ± 5 and M = Pd, −756.9 ± 13 kJ mol^{-1}. Mean bond dissociation energies, $\bar{D}$(M–pd) (kJ mol^{-1}), have been calculated as M = Ni, 377 ± 9 and M = Pd, 299 ± 16.

INTRODUCTION

The pentanedionato radical (pd), $CH_3COCH{=}C(CH_3)O^{\cdot}$, bonds to nickel, palladium and platinum through both of the oxygen atoms to form complexes of the type M(pd)$_2$. The enthalpy, $\Delta H(1)$, of reaction (1)

$$M(pd)_2(g) + 2H(g) \rightarrow M(g) + 2Hpd(g, enol) \quad (1)$$

which may be calculated if the value of $\Delta H_f^0\{M(pd)_2, g\}$ is known, can be equated to the difference between bond dissociation energies, $\Delta H(1) = 2\bar{D}(M\text{–}pd) - 2\bar{D}(H\text{–}pd)$, where $\bar{D}$ refers to the mean value for the dissociation of two pentanedionato radicals. We are interested to discover the trend in $\bar{D}$(M–pd) values with the metals Ni, Pd and Pt. A value $\Delta H_f^0\{Pt(pd)_2, cr\} = -687 \pm 5$ kJ mol^{-1} has been published recently [1], but there is no value for the corresponding Pd(pd)$_2$. Published values of $\Delta H_f^0\{Ni(pd)_2, cr\}$ differ widely. Kąkołowicz and Giera [2] give −910.6 ± 2.1 kJ mol^{-1}, whilst Irving and Ribeiro da Silva [3] give −870.3 ± 3.0 kJ mol^{-1}. In view of this discrepancy, we have redetermined the enthalpy of formation of Ni(pd)$_2$ and also obtained a value for Pd(pd)$_2$ by solution calorimetry. Reaction occurs rapidly between Ni(pd)$_2$ and 1.0 M HCl, but with Pd(pd)$_2$ reaction is rapid only when the concentration of HCl is increased to 11 M.

The enthalpy, $\Delta H(2) = +34.3 \pm 3.0$ kJ mol^{-1}, of reaction (2) has been determined from the relation $\Delta H(2) = \Delta H(3) - 2\Delta H(4) - \Delta H(5)$, where

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$\Delta H(3)$ to $\Delta H(5)$ are the enthalpies of reactions (3) to (5), which have been determined as $\Delta H(3) = -44.5 \pm 2.0$ kJ mol^{-1}, $\Delta H(4) = -0.28 \pm 0.05$ kJ mol^{-1} of Hpd, and $\Delta H(5) = -78.2 \pm 3.0$ kJ mol^{-1}.

$$\mathrm{Ni(pd)_2(cr) + 278[HCl, 54.37\ H_2O](sln)}$$
$$\rightarrow \mathrm{2Hpd(l) + NiCl_2(cr) + 276[HCl, 54.76\ H_2O](sln)} \qquad (2)$$
$$\mathrm{Ni(pd)_2(cr) + 278[HCl, 54.37\ H_2O](sln) \rightarrow solution\ A} \qquad (3)$$
$$\mathrm{2Hpd(l) + 276[HCl, 54.76\ H_2O](sln) \rightarrow solution\ B} \qquad (4)$$
$$\mathrm{NiCl_2(cr) + solution\ B \rightarrow solution\ A} \qquad (5)$$

Using the following ΔH_f^0 values: Hpd(l), -425.5 ± 1.0 kJ mol^{-1} [4]; $NiCl_2$(cr), -305.3 ± 0.1 kJ mol^{-1} [5]; [HCl in 54.76 H_2O](sln), -165.363 kJ mol^{-1} [6]; [HCl in 54.37 H_2O](sln), -165.359 kJ mol^{-1} [6], we calculate the value $\Delta H_f^0\{\mathrm{Ni(pd)_2, cr}\} = -861.0 \pm 5$ kJ mol^{-1}.

The enthalpy, $\Delta H(6) = -29.1 \pm 10$ kJ mol^{-1}, of reaction (6) has been determined from the relation $\Delta H(6) = 2\Delta H(7) + \Delta H(8) - 2\Delta H(9) - \Delta H(10)$, where $\Delta H(7)$ to $\Delta H(10)$ are the enthalpies of reactions (7) to (10), which have been determined as $\Delta H(7) = +15.7 \pm 1.5$ kJ mol^{-1} of NH_4Cl, $\Delta H(8) = -45.3 \pm 1.5$ kJ mol^{-1}, $\Delta H(9) = -8.3 \pm 1.5$ kJ mol^{-1} of Hpd, and $\Delta H(10) = +31.8 \pm 3.4$ kJ mol^{-1}.

$$\mathrm{Pd(pd)_2(cr) + 2NH_4Cl(cr) + 3002[HCl, 3.673\ H_2O](sln)}$$
$$\rightarrow \mathrm{2Hpd(l) + (NH_4)_2PdCl_2(cr) + 3000[HCl, 3.675\ H_2O](sln)} \qquad (6)$$
$$\mathrm{2NH_4Cl(cr) + 3002[HCl, 3.673\ H_2O](sln) \rightarrow solution\ A} \qquad (7)$$
$$\mathrm{Pd(pd)_2(cr) + solution\ A \rightarrow solution\ B} \qquad (8)$$
$$\mathrm{2Hpd(l) + 3000[HCl, 3.675\ H_2O](sln) \rightarrow solution\ C} \qquad (9)$$
$$\mathrm{(NH_4)_2PdCl_2(cr) + solution\ C \rightarrow solution\ B} \qquad (10)$$

Using the following ΔH_f^0 values: Hpd(l), -425.5 ± 1.0 kJ mol^{-1} [4]; $(NH_4)_2PdCl_2$(cr), -841.0 ± 1.1 kJ mol^{-1} [7]; NH_4Cl(cr), -314.33 kJ mol^{-1} [5]; [HCl in 3.675 H_2O](sln), -151.5837 kJ mol^{-1} [6]; [HCl in 3.673 H_2O](sln), -151.5754 kJ mol^{-1} [6], we calculate the value $\Delta H_f^0\{\mathrm{Pd(pd)_2, cr}\} = -756.9 \pm 13$ kJ mol^{-1}.

EXPERIMENTAL

$Ni(pd)_2$ (Koch Light, pure) was dried at 130°C/0.1 mm Hg for 12 h, which converts the light-green dihydrate to the darker green anhydrous compound. $Pd(pd)_2$ (Johnson Matthey and Aldrich Chemical Co.) was used as supplied. For both $Ni(pd)_2$ and $Pd(pd)_2$ the CH analyses were satisfactory. $NiCl_2$ (Ventron GMBH, pure anhydrous) was dried at 150°C/0.1 mm Hg Over P_2O_5 for 12 h and handled in an N_2 atmosphere.

Enthalpies of solution were measured by use of the LKB solution calorimeter at 298 K.

DISCUSSION

Irving and Ribeiro da Silva [3] have determined the enthalpy $\Delta H(11) = -71.0 \pm 0.3$ kJ mol^{-1}, for reaction (11).

$$\begin{aligned}&Ni(pd)_2(cr) + [H_2SO_4, 53.54\ H_2O](sln)\\&\quad\rightarrow 2Hpd(l) + NiSO_4 \cdot 6H_2O(cr) + 47.54\ H_2O(l) \qquad (11)\end{aligned}$$

In their calculation of $\Delta H_f^0\{Ni(pd)_2, cr\}$ these authors appear to have used the datum $\Delta H_f^0\{[H_2SO_4 \text{ in } 6H_2O](sln)\} = -874.2$ kJ mol^{-1} rather than $\Delta H_f^0\{[H_2SO_4 \text{ in } 53.54\ H_2O](sln)\} = -886.87 \pm 0.01$ kJ mol^{-1} [5]. Using this latter value, together with the following ΔH_f^0 values: $H_2O(l)$, -285.83 ± 0.01 kJ mol^{-1} [8]; Hpd(l), -425.5 ± 1.0 kJ mol^{-1} [4]; $NiSO_4 \cdot 6H_2O(cr)$, -2682.8 ± 0.5 kJ mol^{-1} [5], we calculate $\Delta H_f^0\{Ni(pd)_2, cr\} = -861.9 \pm 3.0$ kJ mol^{-1}. This value is the same, within the experimental error, as that which we have found. It is not obvious to us why the value obtained by Kąkołowicz and Giera differs by 48 kJ mol^{-1}, although it may be connected with the uncertain thermodynamic definition of deliquescent $NiCl_2 \cdot 6H_2O$ which they have used.

Previously, we have reported [9] the determination, by use of a Knudsen effusion technique, of the following values for enthalpies of sublimation, ΔH_{sub}^{298}: $Ni(pd)_2$, 132 ± 10 kJ mol^{-1}; $Pd(pd)_2$, 132 ± 17 kJ mol^{-1}; and $Pt(pd)_2$, 133 ± 9 kJ mol^{-1}. For $Ni(pd)_2$ our value is the same as that found by Ashcroft [10], who also used Knudsen effusion with direct measurement of weight loss from the cell. However, Götze et al. [11] have obtained the value $\Delta H_{sub}^{405} = 95.4$ kJ mol^{-1} by a gas entrainment technique, based on the variation of vapour pressure with temperature, which has been confirmed by Kąkołowicz and Giera [2], using GLC, and also by Irving et al. [12], (Knudson effusion). Neither Kąkołowicz nor Irving specify the temperature to which their data refer. We have found no previous value for $\Delta H_{sub}^{298} Pd(pd)_2$. Al-Takhin et al. [1] have obtained $\Delta H_{sub}^{298} Pt(pd)_2 = 114.4 \pm 2.0$ kJ mol^{-1} by use of high-temperature microcalorimetry. Normally, we would prefer to accept a value for the enthalpy of sublimation which has been obtained directly from calorimetry, rather than that derived from vapour pressure data. However, since calorimetrically determined values are not available for $Ni(pd)_2$ or $Pd(pd)_2$, we have chosen to use our own set of sublimation energies. If it should be shown subsequently that our values are too high, the error is likely to be common to each of the three compounds so that the trend in derived $\bar{D}$(M–pd) values will be independent of these errors. We calculate the $\Delta H_f^0\{M(pd)_2 g\}$ values: $Ni(pd)_2$, -729 ± 15; $Pd(pd)_2$, -625

± 30; and Pt(pd)$_2$, -554 ± 14 kJ mol^{-1}. Incorporating the ΔH_f^0(g) values: H, $+218.00 \pm 0.01$ kJ mol^{-1} [5]; Hpd, g, enol, -384.4 ± 1.3 kJ mol^{-1} [4]; Ni, $+429.7$ kJ mol^{-1} [5]; Pd, $+378.2$ kJ mol^{-1}; and Pt, $+565.3$ kJ mol^{-1} [5], we calculate the following $\Delta H(1)$ values: Ni, -46 kJ mol^{-1}; Pd, -202 kJ mol^{-1}; and Pt, -86 kJ mol^{-1}. Using the value D(H–pd) = 400 ± 20 kJ mol^{-1} [13], we obtain the values $\bar{D}$(Ni–pd) = 377 ± 9 kJ mol^{-1}, $\bar{D}$(Pd–pd) = 299 ± 16 kJ mol^{-1} and $\bar{D}$(Pt–pd) = 357 ± 8 kJ mol^{-1} (note that the uncertainty attached to D(H–pd) has not been included in the $\bar{D}$(M–pd) values). Thus the trend in $\bar{D}$(M–pd) values is Ni > Pt > Pd. Our finding that $\bar{D}$(Pt–pd) > $\bar{D}$(Pd–pd) is consistent with the work of Al-Takhin et al. [14] who have determined enthalpies of the gas-phase reactions (12) as follows: L = triphenylphosphine, M = Pd, 753 ± 22, Pt, 986 ± 21 kJ mol^{-1}; L = cyclooctadiene, M = Pd, 769 ± 20, Pt, 978 ± 22 kJ mol^{-1}. In these complexes, platinum bonds more strongly than palladium.

$$ML_2Cl_2(g) \rightarrow M(g) + 2L(g) + 2Cl(g) \qquad (12)$$

The molecular structure of Ni(pd)$_2$ in the gas phase has been determined from electron diffraction studies [15], to yield an Ni–O bond length of 1.876(5) Å in the square planar structure. In crystalline [Ni(pd)$_2$]$_3$ the nickel is six-coordinate and the Ni–O bond length is increased to 2.02 Å [16]. Only the crystal structures of Pd(pd)$_2$ [17] and Pt(pd)$_2$ [18] are available; both are square planar. The bond lengths are Pd–O, 1.96(1) Å and Pt–O, 1.99(1) Å. The Pt(pd)$_2$ molecules are well separated in the crystal, but the structure of Pd(pd)$_2$ shows weak intermolecular interaction, Pd $\cdots$ C$_3$ (3.35 Å), so that the square planar coordination of the metal may be extended to a distorted octahedral coordination. The metal–oxygen bond lengths in the gas phase molecules may differ from those in the crystal. In the absence of these data it is difficult to make a proper comparison between bond length and bond strength in these complexes.

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