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Standard enthalpies of formation of gaseous dicyclopentadienyl-molybdenum and -tungsten dihydrides

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Abstract

The enthalpies of sublimation of the complexes $M(\eta^5\text{-}C_5H_5)_2H_2$ (M = Mo, W) were determined from pressure-temperature data obtained with Knudsen cells. Independent measurements made in Lisbon and in Leeds for the molybdenum complex gave a value for ΔH_s^0 of 82 ± 2 kJ/mol. A value of 84.1 ± 1.6 kJ/mol was derived from measurements in Lisbon for the tungsten analogue. The Mo–H and the W–H mean bond dissociation enthalpies were reevaluated as 256 ± 8 kJ/mol and 311 ± 4 kJ/mol, respectively, on the basis of the new values for ΔH_s^0.

Introduction

Most of the information available on the bond strengths between transition metals and ligands in coordinatively saturated complexes has come from calorimetric measurements of the enthalpy changes which accompany reactions of the compounds concerned [1–5]. In many of these studies the metal–ligand bond enthalpies were derived directly from the reaction enthalpies in solution, by assuming that the solvation enthalpies of the reactants and products are similar. While there is some evidence that this approximation is often reasonable [2], the number of cases for which it can be thoroughly checked is very small, mainly because the available data for enthalpies of sublimation of organometallic complexes are rather scarce. Gas phase metal–ligand bond enthalpies can also be calculated from the enthalpies of formation of the crystalline complexes, obtained by calorimetry [1–5], but again the method requires values of the enthalpies of sublimation of the compounds.

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The lack of reliable enthalpies of sublimation of organometallic complexes is related to the difficulty of measuring these quantities: many complexes have a very low vapour pressure at room temperature and decompose on heating. It may be difficult also to estimate values of enthalpies of sublimation unless information is available for complexes of similar structure.

The thermochemistry of a large series of complexes of the type $M(Cp)_2L_2$ ($M = Ti$, Mo, W; $Cp = \eta^5\text{-}C_5H_5$; $L = H$, alkyl, aryl, halogen, etc.) has been investigated [6]. For most of these molecules, the derived metal–ligand mean bond dissociation enthalpies rely on enthalpies of sublimation which were estimated on the basis of experimental data for a few of them. Although values are available for the molybdenum and tungsten dihydrides [7], these compounds are difficult to study since they are sensitive to oxygen. We decided to remeasure their enthalpies of sublimation, with a view to improving the accuracy of the values of the Mo–H and W–H bond enthalpies.

Experimental

The molybdenum and tungsten dihydride complexes were prepared as described by Green and Knowles [8]. The compounds were kept under argon or nitrogen and were resublimed before the vapour pressure measurements.

The measurements in Leeds [9] depend on monitoring the mass loss from the sample due to Knudsen effusion. Simultaneously, the torsional deflection of the cell suspension is measured by optical means. The advantage of the combined method is due to the fact that the relationship between mass loss and vapour pressure depends on the molar mass of the species leaving the hole, whereas the torsional deflection method depends only on the torsional characteristics of the suspension. Agreement between the vapour pressures measured by the two methods would confirm that the assumed value of the molar mass was correct. The torsional Knudsen effusion recoil method is known by the acronym *torker*.

In the work on the molybdenum compound, effusion through two holes of diameters (200 ± 5) μ and (400 ± 10) μ was studied. The holes were drilled by laser in stainless steel of $(13 \pm 0.5) \times 10^{-4}$ cm thickness. These dimensions correspond with the Clausing correction factors (which allow for non-specular collisions with the walls of the orifice) of 0.939 ± 0.010 and 0.969 ± 0.010 respectively. In the torker technique the geometrical factor that takes account of for the finite thickness of the hole is somewhat greater than the Clausing value (0.955 ± 0.010; 0.972 ± 0.012) because the force depends on the angular distribution of the effusing molecules as well as on their number. These correction factors have been tabulated and discussed [9–11]. It is an advantage to use holes of different diameters because other sources of error may be revealed, such as self-cooling of the sample, an unsatisfactory hole diameter-mean free path ratio, or deviations from the assumed absolute vacuum on the low pressure side of the hole.

The Leeds mass loss measurements of pressure were based on eq. 1, where W is the rate of mass loss, p the pressure, K_c the Clausing correction calculated by the De Marcus equation [9], A the hole area, M the molar mass of the effusing species, R the gas constant, and T the absolute temperature.

$$W = pK_cA\left(\frac{M}{2\pi RT}\right)^{1/2} \qquad (1)$$

In the torker technique p is given by eq. 2, where D is the torsional constant of the wire, θ the angle of optical deflection, f the geometrical factor, and l the distance from the hole to the suspension system. As stated above, agreement between the two methods of measurement confirms the correctness of the assumed molar mass.

$$p = \frac{D\theta}{flA} \tag{2}$$

Equations 1 and 2 are based on the assumption of free molecular flow, which holds when the ratio r/λ is close to zero, where λ is the mean free path of the molecules in the cell. Hiby and Pahl [12–14] have discussed the situation in which r/λ is not zero and suggested that an additional term, $(1 + 0.24r/\lambda)^{-1}$, should be included in the equation for p. The introduction of this pressure-sensitive term may alter the slope of the pressure-temperature plot and give a different value for the enthalpy of sublimation. Usually free molecular flow conditions are satisfactory if $\lambda/2r$ is at least 10, and it is noteworthy that Edwards and Kington [14], using holes for which λ was in the range $2r$–$10r$, found that the derived value of the enthalpy of sublimation of ferrocene was lowered by 3.4 kJ/mol when the above term was introduced in eq. 1.

The mean free path of the molybdenum complex was based on the collision diameter of this molecule, which was estimated to be 749 pm from the Van der Waals radii [15] and projections of its molecular structure [16] on the x, y, z planes. The dimensions of the Leeds effusion holes were such that the Hiby and Pahl factor made no significant difference to the derived enthalpy of sublimation (see Discussion). In the 200 μ cell the vapour pressure was measured in the temperature range 297.87–345.61 K and varied from 0.0143 to 1.6538 Pa. When the 400 μ hole was used the temperature range was 298.95–357.21 K and the vapour pressure varied from 0.0167 to 4.2737 Pa.

The Lisbon mass loss vapour pressure measurements were made by use of a bronze cell with a hole of diameter 0.1076 cm drilled in a 2.09×10^{-3} cm thick copper foil, which was soldered to the cell lid [17*]. The temperature was controlled to ±0.01 K using a Haake ED Unitherm thermostat and measured to ±0.01 K with a calibrated mercury thermometer. The mass loss was measured by weighing the cell to $\pm 10^{-5}$ g with a Sartorius 2474 balance.

The vapour pressures of the molybdenum and tungsten complexes were calculated from eq. 1. The Clausing factor $K_c = 0.986$ was obtained from the relationship $K_c = 8r/(3L + 8r)$, where L and r are the thickness and the radius of the hole, respectively [10,17*]. As in the case of the Leeds cell, the value of $\lambda/2r$ was sufficiently large for this factor to make a small difference to the derived values of the enthalpies of sublimation (see Discussion). The vapour pressure in Lisbon was studied over the temperature ranges 302.74–311.85 K (molybdenum complex) and 313.53–322.68 K (tungsten complex), and varied from 0.0172–0.0438 Pa and 0.0243–0.0597 Pa, respectively.

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* Reference number with asterisk indicates a note in the list of references.

Table 1

Parameters A and B for eq. 3 and values of the standard enthalpies of sublimation (kJ/mol) for the molybdenum and tungsten complexes

Complex	Method [a]	A	$B \times 10^{-3}$	ΔH_s^0
$Mo(Cp)_2H_2$	ML(1)	29.889 ± 0.330	−10.149 ± 0.104	84.4 ± 0.9
	T(1)	30.274 ± 0.240	−10.199 ± 0.076	84.8 ± 0.6
	ML(2)	29.592 ± 0.262	−10.065 ± 0.083	83.7 ± 0.7
	T(2)	30.286 ± 0.235	−10.205 ± 0.122	84.8 ± 1.0
	ML(3)	27.783 ± 0.443	−9.643 ± 0.137	80.2 ± 1.1
$W(Cp)_2H_2$	ML(3)	28.625 ± 0.625	−10.146 ± 0.199	84.4 ± 1.7

[a] ML(1) ≡ Mass loss (Leeds), 200 μ hole; mean temperature 315.78 K. T(1) ≡ Torker (Leeds), 200 μ hole; mean temperature 318.95 K. ML(2) ≡ Mass loss (Leeds), 400 μ hole; mean temperature 317.25 K. T(2) ≡ Torker (Leeds), 40 μ hole; mean temperature 317.82 K. ML(3) ≡ Mass loss (Lisbon); mean temperatures 307.30 (Mo) and 318.11 K (W).

Results and discussion

The vapour pressure-temperature data were fitted to eq. 3 by the least squares method. The values obtained for A and B are shown in Table 1, together with the values derived for the enthalpies of sublimation.

$$\ln(p/\mathrm{Pa}) = A + B/\mathrm{T} \tag{3}$$

The constants A and B in Table 1 can be used to calculate the vapour pressure of the molybdenum complex at 300 K. The experiments in Leeds yield:

Mass loss,	200 μ,	$p = 0.0194$ Pa;
Torker,	200 μ,	$p = 0.0242$ Pa;
Mass loss,	400 μ,	$p = 0.0191$ Pa;
Torker,	400 μ,	$p = 0.0240$ Pa.

The small difference between the mass loss and the torker values, 0.005 Pa, is due to a zero point error in measuring the angle of deflection. The close agreement between the mass loss and the torker slopes confirmed that the effusate had the assumed molar mass.

The experimental set-up in Lisbon cannot yield reliable values of vapour pressures in the range of 10^{-2} Pa because the pressure in the vacuum chamber enclosing the Knudsen cell is not lower than 0.7×10^{-2} Pa. This implies that the vapour pressure obtained with eq. 1 (where p is actually a difference between the pressures inside and outside the cell) are lower limits of the true values. Indeed the result derived through eq. 3 ($T = 300$ K) and the constants A and B from Table 1, $p = 0.0128$ Pa, is about 0.7×10^{-2} lower than the more accurate mass loss value measured in Leeds.

Although there is a difference between the Leeds and Lisbon values for the enthalpy of sublimation of the molybdenum dihydride, it appears that the previous published value, 92.5 ± 2.1 kJ/mol [18], is too high. The same can be said in the case of the tungsten dihydride, for which Tel'noi et al. reported a value of 96.2 ± 2.1 kJ/mol [18]. These discrepancies may have been due to the oxygen-sensitivity of the bright yellow complexes; a small amount of decomposition produces a brown layer on the surface of the powder which inhibits sublimation. This may account also for the difference between the Leeds and Lisbon values for the molybdenum complex. The agreement in the results from both laboratories is improved, however, when the Hiby and Pahl correction is taken into account (see Experimental section): the Leeds values fall by 0.9 kJ/mol but the Lisbon value by only ca. 0.2 kJ/mol. The correction applied to the tungsten dihydride leads to a 0.3 kJ/mol decrease.

By use of a mean value of the Leeds and Lisbon results for the molybdenum complex, $\Delta H_s^0 = 82 \pm 2$ kJ/mol, and of the calorimetric result for ΔH_f^0[Mo(Cp)$_2$H$_2$,c], 210.3 ± 5.7 kJ/mol [6], the standard enthalpy of formation of the gaseous molecule is calculated as $\Delta H_f^0[\mathrm{Mo(Cp)_2H_2,g}] = 292.3 \pm 6.0$ kJ/mol. For the tungsten complex, the enthalpy of sublimation in Table 1 and $\Delta H_f^0[\mathrm{W(Cp)_2H_2,c}] = 222.4 \pm 8.8$ kJ/mol [6], yield $\Delta H_f^0[\mathrm{W(Cp)_2H_2,g}] = 306.8 \pm 9.0$ kJ/mol.

The methods and approximations used to evaluate metal–ligand bond strengths from the standard enthalpies of formation of organometallic complexes have been recently discussed [2]. In the case of bis(cyclopentadienyl)molybdenum and tungsten complexes, the metal–ligand mean bond dissociation enthalpies, $\bar{D}$(M–L), can be estimated (eq. 5) by considering the enthalpy of reaction 4. This requires, however, that the enthalpies of formation of the gaseous dichloride complexes and $\bar{D}$(M–Cl) are available. While this is so for the enthalpies of formation of the crystalline compounds M(Cp)$_2$Cl$_2$ (M = Mo, W) [6,18], their enthalpies of sublimation have not been determined. (Attempts in Leeds to measure these quantities were unsuccessful.) Estimates of $\Delta H_s^0[\mathrm{Mo(Cp)_2Cl_2}] = 100.4 \pm 4.2$ kJ/mol and $\Delta H_s^0[\mathrm{W(Cp)_2Cl_2}] = 104.6 \pm 4.2$ kJ/mol have been reported [6,18] and were used to derive the enthalpy of reaction 4 for L = H: −95.1 kJ/mol (M = Mo) and −73.1 kJ/mol (M = W). The remaining information needed to calculate $\bar{D}$(M–L) are the metal–chlorine mean bond dissociation enthalpies, which unfortunately are also not available. The method used to solve this problem consists in identifying $\bar{D}$(M–Cl) in the complexes with $\bar{D}$(M–Cl) in the homoleptic compounds MoCl$_6$ and WCl$_6$, 303.8 ± 7.1 kJ/mol and 347.3 ± 0.8 kJ/mol, respectively [6]. This finally leads to $\bar{D}(\mathrm{Mo{-}H}) = 256 \pm 8$ kJ/mol and $\bar{D}(\mathrm{W{-}H}) = 311 \pm 4$ kJ/mol. It must be emphasized that although inaccurate estimates of the enthalpies of sublimation of the dichlorides or the assignment of less reliable values to $\bar{D}$(M–Cl) would affect the above results for $\bar{D}$(M–H), these errors will be constant in a series of metal–ligand mean bond dissociation enthalpies determined by the same method [6].

$$\mathrm{Mo(Cp)_2L_2(g) + 2Cl(g) \rightarrow Mo(Cp)_2Cl_2(g) + 2L(g)} \qquad (4)$$

$$\Delta H = 2\bar{D}(\mathrm{M{-}L}) - 2\bar{D}(\mathrm{M{-}Cl}) \qquad (5)$$

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