Journal of Organometallic Chemistry, 222 (1981) 69—78
Elsevier Sequoia S.A., Lausanne — Printed in The Netherlands

ENTHALPIES OF FORMATION OF $Ti(\eta\text{-}C_5H_5)_2(OR)_2$ COMPLEXES (R = C_6H_5, $2\text{-}CH_3C_6H_4$, $3\text{-}CH_3C_6H_4$, $4\text{-}CH_3C_6H_4$, AND $2\text{-}ClC_6H_4$)

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(Received July 10th, 1981)

Summary

The standard enthalpies of formation of the title crystalline complexes at 298.15 K have been determined by reaction-solution calorimetry. The results give $\Delta H_f^0[Ti(\eta\text{-}C_5H_5)_2(OC_6H_5)_2,c] = -379.2 \pm 8.0$, $\Delta H_f^0[Ti(\eta\text{-}C_5H_5)_2(2\text{-}CH_3C_6H_4O)_2,c] = -416.7 \pm 8.1$, $\Delta H_f^0[Ti(\eta\text{-}C_5H_5)_2(3\text{-}CH_3C_6H_4O)_2,c] = -393.6 \pm 8.1$, $\Delta H_f^0[Ti(\eta\text{-}C_5H_5)_2(4\text{-}CH_3C_6H_4O)_2,c] = -416.5 \pm 7.8$, and $\Delta H_f^0[Ti(\eta\text{-}C_5H_5)_2(2\text{-}ClC_6H_4O)_2,c] = -407.6 \pm 21.5$ kJ mol^{-1}. The metal—oxygen bond strengths have been evaluated as mean bond-disruption enthalpies ($\bar{D}$) and as mean bond-enthalpy terms ($\bar{E}$). The method of calculation of these values is analysed and earlier relevant thermochemical data are reviewed.

Introduction

The aim of our thermochemical studies on $M(\eta\text{-}C_5H_5)_2L_2$ complexes (M = transition metal atom; L = ligand) has been the evaluation of M—L bond strengths and their correlation with other physical-chemical parameters or with reactivity data. For example, in a recent paper [1] we considered the influence of the nature of chemical groups in the ligands on the M—L bond strength.

In the course of these studies several problems have arisen, some of them impossible to solve at the present state of knowledge. First, the paucity of good quality auxiliary thermochemical data precludes conclusions from more precise bond strength results. To our knowledge enthalpies of formation of simple molecules such as carbon tetrabromide and bromoform, and enthalpies of sublimation of substances such as 2-chlorophenol, have never been measured accurately. Thus their estimated values usually have large uncertainty intervals.

The difficulty of estimating enthalpies of sublimation of organometallic complexes, which is often necessary, is another important source of inaccuracy and lack of precision. Nevertheless this problem is less serious; it may be diffi-

0022-328X/81/0000—0000/$02.50

cult to find a reliable value for $\Delta H_s^0[M(\eta\text{-}C_5H_5)_2L_2]$, but once this is obtained it is usually much easier to calculate ΔH_s^0 for an analogous complex, $M(\eta\text{-}C_5H_5)_2L'_2$. Therefore, although the precision and accuracy of the "absolute" bond strengths are significantly decreased by the uncertainties associated with ΔH_s^0 of both complexes this is not the case for the relative bond strengths.

A third difficulty which must be mentioned, since it is often a major source of error in bond strength results, is the scarcity of good values for many bond dissociation enthalpies, D(L—H), from which the enthalpies of formation of radicals are evaluated. In some cases it is even useless to try to estimate a bond dissociation enthalpy, bearing in mind the range of uncertainty.

The present paper, being a "mise-au-point" of bond strength values obtained so far in our group, illustrates all the problems mentioned above. The calculation of thermochemical parameters, usually regarded as measurements of bond strengths (mean bond-disruption enthalpies, $\bar{D}$, and mean bond-enthalpy terms, $\bar{E}$), is discussed, and an attempt is made to evaluate $\bar{E}$(M—L) for each of the complexes. Finally, the results of thermochemical studies of $Ti(\eta\text{-}C_5H_5)_2(OR)_2$ complexes (R = C_6H_5, 2-$CH_3C_6H_4$, 3-$CH_3C_6H_4$, 4-$CH_3C_6H_4$ and 2-ClC_6H_4) are presented.

Experimental

Calorimeter

The reaction and solution enthalpies were measured in the reaction-solution calorimeter previously described [2]. There was no need to make the thermochemical measurements under nitrogen because all the compounds involved are fairly air-stable.

Compounds

Complexes $Ti(\eta\text{-}C_5H_5)_2(OR)_2$ (R = C_6H_5, 2-$CH_3C_6H_4$, 3-$CH_3C_6H_4$, 4-$CH_3C_6H_4$, and 2-ClC_6H_4) were prepared and purified as described by Andrä [3]. The reaction solutions were prepared from Merck p.a. hydrochloric acid and acetone, which were used without any further treatment. B.D.H. AnalaR phenol was recrystalized from 40—60 petroleum ether. Fluka 2-methylphenol, 3-methylphenol, and 4-methylphenol were purified as described in the literature [4]. Fluka 2-chlorophenol was distilled several times and its purity was confirmed by its refractive index.

Reactions

The solutions used in the thermochemical studies of reactions 1 were mix-

$$Ti(\eta\text{-}C_5H_5)_2(OR)_2\ (c) + 2\ HCl\ (soln) \rightarrow Ti(\eta\text{-}C_5H_5)_2Cl_2\ (soln) + 2\ ROH\ (soln) \quad (1)$$

tures of aqueous hydrochloric acid and acetone. With R = C_6H_5 and 3-$CH_3C_6H_4$ a 1:1 mixture of 8.3 mol dm^{-3} aqueous HCl and acetone was used (solution A); with R = 2-$CH_3C_6H_4$, 4-$CH_3C_6H_4$, and 2-ClC_6H_4 it was necessary to use a 1:4 mixture of 10.0 mol dm^{-3} aqueous HCl and acetone (solution B). The disadvantages of these mixtures from a thermochemical point of view were discussed previously [1].

The products of reactions 1 were confirmed by IR spectroscopic analysis.

TABLE 1

THERMOCHEMICAL RESULTS (kJ mol^{-1}) FOR REACTION 1

$Ti(\eta\text{-}C_5H_5)_2(OR)_2$	R				
	C_6H_5	$2\text{-}CH_3C_6H_4$	$3\text{-}CH_3C_6H_4$	$4\text{-}CH_3C_6H_4$	$2\text{-}ClC_6H_4$
ΔH_r	20.3 ± 1.1	3.3 ± 1.2	−42.7 ± 2.1	9.90 ± 0.26	2.56 ± 0.94
ΔH_{d1}	5.2 ± 1.8	17.2 ± 1.3	5.2 ± 1.8	17.2 ± 1.3	17.2 ± 1.3
ΔH_{d2}	12.09 ± 0.61	8.29 ± 0.56	2.40 ± 0.29	6.43 ± 0.22	−11.13 ± 0.55

TABLE 2

ENTHALPIES OF FORMATION, ΔH_f^0 (c) AND ΔH_f^0 (g) IN kJ mol^{-1}

$Ti(\eta\text{-}C_5H_5)_2(OR)_2$	R				
	C_6H_5	$2\text{-}CH_3C_6H_4$	$3\text{-}CH_3C_6H_4$	$4\text{-}CH_3C_6H_4$	$2\text{-}ClC_6H_4$
ΔH_f^0 (c)	−379.2 ± 8.0	−416.7 ± 8.1	−393.6 ± 8.1	−416.5 ± 7.8	−407.6 ± 21.5
ΔH_s^0	97 ± 8 [e]	104 ± 8 [e]	104 ± 8 [e]	104 ± 8 [e]	90 ± 10 [e]
ΔH_f^0 (g)	−282.2 ± 11.3	−312.7 ± 11.4	−289.6 ± 11.4	−312.5 ± 11.2	−317.6 ± 23.7

[e] Estimated value.

All reaction and solution enthalpies presented are mean values from five independent experiments, and refer to 298.15 K. The uncertainties are twice the standard deviation of the mean in each case.

Auxiliary data

Standard enthalpies of formation and vaporization at 298 K were used in evaluating the thermochemical results (values in kJ mol^{-1}): ΔH_f^0(HCl, soln A) = —162.47 ± 0.28 [1]; ΔH_f^0(HCl, soln B) = —172.59 ± 0.51 [1]; ΔH_f^0(C_6H_5OH,c) = —165.0 ± 0.7 [5]; ΔH_f^0(2-$CH_3C_6H_4OH$,c) = —204.6 ± 1.0 [5]; ΔH_f^0(3-$CH_3C_6H_4$-OH,l) = —194.0 ± 0.6 [5]; ΔH_f^0(4-$CH_3C_6H_4OH$,c) = —199.3 ± 0.7 [5]; ΔH_f^0-[Ti(η-$C_5H_5)_2Cl_2$,c] = —383.2 ± 7.5 [6]; ΔH_s^0(C_6H_5OH) = 68.7 ± 0.5 [5]; ΔH_s^0-(2-$CH_3C_6H_4OH$) = 76.0 ± 0.8 [5]; ΔH_v^0(3-$CH_3C_6H_4OH$) = 61.7 ± 1.0 [5]; ΔH_s^0-(4-$CH_3C_6H_4OH$) = 73.9 ± 1.5 [5]; ΔH_f^0(Cl,g) = 121.302 ± 0.008 [7]; ΔH_s^0-[Ti(η-$C_5H_5)_2Cl_2$] = 118.8 ± 2.1 [6]; ΔH_f^0(H,g) = 217.997 ± 0.006 [7]. The standard enthalpy of formation of liquid 2-chlorophenol was estimated as —181 ± 10 kJ mol^{-1} and its enthalpy of vaporization as 36 ± 4 kJ mol^{-1}. It was assumed that D(RO—H) = D(C_6H_5O—H) = 362 ± 10 kJ mol^{-1} [8].

Results

The thermochemical results are summarized in Table 1, where ΔH_r represents the enthalpy of reaction 1. ΔH_{d1} refers to the enthalpy of solution of Ti(η-$C_5H_5)_2Cl_2$ (c) in solution A or B and ΔH_{d2} stands for the enthalpy of solution of ligands ROH in solution A or B containing stoicheiometric amounts of Ti(η-$C_5H_5)_2Cl_2$.

The standard enthalpies of formation of the crystalline complexes (Table 2) were derived by using the above results and the appropriate auxiliary data. Estimated values of the enthalpies of sublimation and results for ΔH_f^0(g) are also listed in Table 2.

Discussion

The evaluation of mean bond-disruption enthalpies, $\bar{D}$(M—L), in complexes M(η-$C_5H_5)_2L_2$ (M = transition metal; L = mono- or polyatomic ligand) was based on the assumption that values of $\bar{D}$(M—Cl) in M(η-$C_5H_5)_2Cl_2$ are equal to the mean bond dissociation enthalpies in MCl_n (n = 4 for M = Ti and n = 6 for M = Mo, W) [1,2,9—13]. This assumption is supported by similarities between internuclear distances of M—Cl bonds in the complexes and in MCl_n compounds [6]. However, the calculation also involves several other assumptions which must be considered carefully when these bond enthalpies are derived.

The mean bond-enthalpy term, $\bar{E}$(M—L), in a complex M(η-$C_5H_5)_2L_2$ is one half of the enthalpy change associated with the process

$$M(\eta\text{-}C_5H_5)_2L_2\ (g) \rightarrow M(\eta\text{-}C_5H_5)_2^{*}\ (g) + 2\ L^{*}\ (g) \tag{2}$$

$$\Delta H_2 = 2\ \bar{E}(M\text{—}L) \tag{3}$$

where the star indicates that M(η-$C_5H_5)_2^{*}$ and L* structures remain as they were in the complex (i.e., they are non-reorganized fragments).

Considering a second reaction *

$$M(\eta\text{-}C_5H_5)_2Cl_2\,(g) \rightarrow M(\eta\text{-}C_5H_5)_2^*\,(g) + 2\,Cl\,(g) \tag{4}$$

$$\Delta H_4 = 2\,\bar{E}(M{-}Cl) \tag{5}$$

and subtracting ΔH_4 from ΔH_2 we arrive at

$$\Delta H_2 - \Delta H_4 = 2\,\bar{E}(M{-}L) - 2\,\bar{E}(M{-}Cl) = 2\,\Delta H_f^0(L^*,g) - 2\,\Delta H_f^0(Cl,g)$$
$$- \Delta H_f^0[M(\eta\text{-}C_5H_5)_2L_2,g] + \Delta H_f^0[M(\eta\text{-}C_5H_5)_2Cl_2,g] \tag{6}$$

if it is assumed that the species $M(\eta\text{-}C_5H_5)_2^*$ (g) are similar in both reactions 2 and 4. As we will show, this can be partially verified if the crystal structures of $M(\eta\text{-}C_5H_5)_2L_2$ and $M(\eta\text{-}C_5H_5)_2Cl_2$ complexes are available.

In terms of $\bar{D}$, the mean bond-disruption enthalpy, we have

$$M(\eta\text{-}C_5H_5)_2L_2\,(g) \rightarrow M(\eta\text{-}C_5H_5)_2\,(g) + 2\,L\,(g) \tag{7}$$

$$\Delta H_7 = 2\,\bar{D}(M{-}L) \tag{8}$$

$$M(\eta\text{-}C_5H_5)_2Cl_2\,(g) \rightarrow M(\eta\text{-}C_5H_5)_2\,(g) + 2\,Cl\,(g) \tag{9}$$

$$\Delta H_9 = 2\,\bar{D}(M{-}Cl) \tag{10}$$

$$\Delta H_7 - \Delta H_9 = 2\,\bar{D}(M{-}L) - 2\,\bar{D}(M{-}Cl) = 2\,\Delta H_f^0(L,g) - 2\,\Delta H_f^0(Cl,g)$$
$$- \Delta H_f^0[M(\eta\text{-}C_5H_5)_2L_2,g] + \Delta H_f^0[M(\eta\text{-}C_5H_5)_2Cl_2,g] \tag{11}$$

The difference

$$(\Delta H_7 - \Delta H_9) - (\Delta H_2 - \Delta H_4) = 2\,\Delta H_f^0(L,g) - 2\,\Delta H_f^0(L^*,g) = 2\,ER(L^*) \tag{12}$$

leads to $ER(L^*)$, the reorganization enthalpy of L.

As stated above it has been assumed that $\bar{D}(M{-}Cl)$ in MCl_n (in this particular case equal to $\bar{E}(M{-}Cl)$) is similar to $\bar{D}(M{-}Cl)$ in $M(\eta\text{-}C_5H_5)_2Cl_2$. However it is known that only $\bar{E}$ values can be safely correlated with bond distances, particularly when large reorganization enthalpies are involved. Therefore the correct assumption must be

$$\bar{D}(M{-}Cl) = \bar{E}(M{-}Cl) \text{ in } MCl_n$$
$$= \bar{E}(M{-}Cl) \text{ in } M(\eta\text{-}C_5H_5)_2Cl_2$$

Writing

$$\bar{D}(M{-}Cl) = \bar{E}(M{-}Cl) \text{ in } M(\eta\text{-}C_5H_5)_2Cl_2$$

implies that $ER[M(\eta\text{-}C_5H_5)_2^*] = 0$, which does not seem plausible.

Our thermochemical studies were concerned with $M(\eta\text{-}C_5H_5)_2L_2$ complexes with M = Mo, W and Ti, and the discussion below is confined to this type of complex. We are not aware of any structural data for $M(\eta\text{-}C_5H_5)_2L_2$ molecules in the gaseous phase. Crystal data are available for some of these complexes. A number of examples from the literature for M = Mo, Ti [14—19] shows that the $(C_5H_5){-}M{-}(C_5H_5)$ ring centroid angles are fairly constant and usually less

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* $\Delta H_f^0(Cl^*,g) = \Delta H_f^0(Cl,g)$ as the reorganization enthalpy for monoatomic species is zero.

than 135° [14]. Bond distances $r(\mathrm{M{-}C_5H_5})$ also vary within a narrow range ($\sim$197 ± 1 pm for M = Mo and $\sim$206 ± 1 pm for M = Ti). Finally, the average cyclopentadienyl ring structures do not seem to vary very much for different $\mathrm{M(\eta\text{-}C_5H_5)_2L_2}$ complexes. Although these data do not refer to the gaseous phase they favour the hypothesis of structural similarity of $\mathrm{M(\eta\text{-}C_5H_5)_2^{\star}}$ fragments and consequently support the calculation method represented by eq. 6.

However, there are a few exceptions to the average values of crystal data mentioned above, particularly when the $\mathrm{(C_5H_5){-}M{-}(C_5H_5)}$ ring centroid angles are considered. These angles are larger when L is a weak π-acceptor and strong σ-donor, as in the case of $\mathrm{Mo(\eta\text{-}C_5H_5)_2H_2}$ (145.8°) [20], $\mathrm{Mo(\eta\text{-}C_5H_5)_2D_2}$ (148.2°) [14] and, to a lesser extent, $\mathrm{Mo(\eta\text{-}C_5H_5)_2(NO)(\sigma\text{-}C_5H_5)}$ (137.6) [14]. The first of these three complexes has already been the subject of thermochemical studies [9] and the mean bond enthalpy term $\bar{E}$(Mo—H) was derived through eq. 6 (see Table 3). Since the ring centroid angle in $\mathrm{M(\eta\text{-}C_5H_5)_2H_2}$ is much larger than in $\mathrm{Mo(\eta\text{-}C_5H_5)_2Cl_2}$ (130.5) [14], then on the basis of the assumption that the reorganization enthalpy of $\mathrm{M(\eta\text{-}C_5H_5)_2^{\star}}$ in the dihydride complex is higher than that of $\mathrm{M(\eta\text{-}C_5H_5)_2^{\star}}$ in the dichloride complex [21], the obtained value for $\bar{E}$(Mo—H) may be high. The same can possibly be said about the tungsten analogues and $\bar{E}$(W—H) (see Table 4), though in this case we are not aware of reported crystal structures for the complexes.

The thermochemical data for complexes $\mathrm{M(\eta\text{-}C_5H_5)_2L_2}$ (M = Mo, W, and Ti) obtained by reaction-solution calorimetry are listed in Tables 3, 4 and 5, respectively. Mean bond-disruption enthalpies ($\bar{D}$) were evaluated through eq. 13 and mean bond-enthalpy terms ($\bar{E}$) were derived with eq. 14. These equations are prefered to eq. 6 and 11 since they do not overestimate the final uncertainty intervals. (Note that eq. 6 and 11 contain twice the uncertainty interval of $\Delta H_f^0(\mathrm{LH,c/l})$, included in $\Delta H_f^0(\mathrm{L^{\star},g})$ or $\Delta H_f^0(\mathrm{L,g})$ and in $\Delta H_f^0[\mathrm{M(\eta\text{-}C_5H_5)_2L_2,g}]$, and also that $\Delta H_f^0(\mathrm{LH,c/l})$ does not appear in eqs. 13 and 14).

$$\begin{aligned}\bar{D}(\mathrm{M{-}L}) - \bar{D}(\mathrm{M{-}Cl}) = {}& (\Delta H_r - \Delta H_{d1} - 2\,\Delta H_{d2})/2 + \{\Delta H_s^0[\mathrm{M(\eta\text{-}C_5H_5)_2Cl_2}] - \Delta H_s^0[\mathrm{M(\eta\text{-}C_5H_5)_2L_2}]\}/2 \\ & + \Delta H_f^0(\mathrm{HCl,soln}) + D(\mathrm{L{-}H}) + \Delta H_v^0(\mathrm{LH}) - \Delta H_f^0(\mathrm{H,g}) - \Delta H_f^0(\mathrm{Cl,g}) \end{aligned} \tag{13}$$

$$\begin{aligned}\bar{E}(\mathrm{M{-}L}) - \bar{E}(\mathrm{M{-}Cl}) = {}& (\Delta H_r - \Delta H_{d1} - 2\,\Delta H_{d2})/2 + \{\Delta H_s^0[\mathrm{M(\eta\text{-}C_5H_5)_2Cl_2}] - \Delta H_s^0[\mathrm{M(\eta\text{-}C_5H_5)_2L_2}]\}/2 \\ & + \Delta H_f^0(\mathrm{HCl,soln}) + E(\mathrm{L{-}H}) + \Delta H_v^0(\mathrm{LH}) - \Delta H_f^0(\mathrm{H,g}) - \Delta H_f^0(\mathrm{Cl,g}) \end{aligned} \tag{14}$$

ΔH_r, ΔH_{d1} and ΔH_{d2} are experimental quantities whose meaning was defined above (see "Results").

Equation 14 implies that the structure of $\mathrm{L^{\star}}$ in LH and in $\mathrm{M(\eta\text{-}C_5H_5)_2L_2}$ must be similar. The paucity of X-ray or neutron diffraction data for the complexes of Tables 3, 4, and 5 mean that this assumption cannot be fully tested. However it can be noticed that, for example in $\mathrm{Ti(\eta\text{-}C_5H_5)_2(pyrrol)_2}$, the average structural parameters of $\mathrm{NC_4H_4}$ fragment do not change much on going from $\mathrm{NC_4H_5}$ to the complex [17,22]. The same can be said for $\mathrm{C_6H_5}$ in $\mathrm{C_6H_6}$ [22] and $\mathrm{Ti(\eta\text{-}C_5H_5)_2(C_6H_5)_2}$ [23].

(Continued on p. 77)

TABLE 3

THERMOCHEMICAL DATA (kJ mol^{-1}) FOR $Mo(\eta\text{-}C_5H_5)_2L_2$ COMPLEXES

Complex	ΔH_f^0 (c)	ΔH_s^0 [a]	ΔH_f^0 (g)	$\overline{D}$(Mo—L)	$\overline{E}$(Mo—L) [b]	Reference
$Mo(\eta\text{-}C_5H_5)_2Cl_2$ [c]	−95.8 ± 2.5	(100.4 ± 4.2)	4.6 ± 4.9	303.8 ± 7.1 [d]	303.8 ± 7.1	6
$Mo(\eta\text{-}C_5H_5)_2Br_2$	8.4 ± 18.3	(100.4 ± 4.2)	108.8 ± 18.8	242 ± 12	242 ± 12	11
$Mo(\eta\text{-}C_5H_5)_2I_2$	69.8 ± 7.8	(100.4 ± 4.2)	170.2 ± 8.9	207 ± 9	207 ± 9	2
$Mo(\eta\text{-}C_5H_5)_2H_2$	210.3 ± 5.7	92.5 ± 2.1	302.8 ± 6.1	251 ± 8	251 ± 8	9
$Mo(\eta\text{-}C_5H_5)_2(CH_3)_2$	283.8 ± 4.0	70.4 ± 4.2	354.2 ± 5.8	155 ± 8	126 ± 11	10, 12
$Mo(\eta\text{-}C_5H_5)_2(OCOC_6H_5)_2$	−486.2 ± 3.4	(94 ± 10)	−392.2 ± 10.6	305 ± 10	320 ± 12	1
$Mo(\eta\text{-}C_5H_5)_2(OCOCF_3)_2$	−1 952.0 ± 3.9	(90 ± 10)	−1 862.0 ± 10.7	300 ± 13	318 ± 12	1
$Mo(\eta\text{-}C_5H_5)_2(S\text{-}n\text{-}C_3H_7)_2$	4.6 ± 5.3	(90 ± 10)	94.6 ± 11.3	237 ± 13	213 ± 12	13
$Mo(\eta\text{-}C_5H_5)_2(S\text{-}i\text{-}C_3H_7)_2$	57.1 ± 5.7	(90 ± 10)	147.1 ± 11.5	202 ± 13	178 ± 12	13
$Mo(\eta\text{-}C_5H_5)_2(S\text{-}n\text{-}C_4H_9)_2$	14.0 ± 5.7	(92 ± 10)	106.0 ± 11.5	211 ± 13	186 ± 12	13
$Mo(\eta\text{-}C_5H_5)_2(S\text{-}t\text{-}C_4H_9)_2$	6.9 ± 4.4	(92 ± 10)	98.9 ± 10.9	193 ± 12	168 ± 12	13
$Mo(\eta\text{-}C_5H_5)_2(SC_6H_5)_2$	273.7 ± 4.3	(95 ± 10)	368.7 ± 10.9	238 ± 11	255 ± 12	32

[a] Estimated values in brackets.

[b] The uncertainty assigned to each laidler parameter is ±8 kJ mol^{-1}.

[c] Combustion calorimetry data.

[d] Value subject to an error equal to $ER[M(\eta\text{-}C_5H_5)_2^*]/2$ (see text).

TABLE 4

THERMOCHEMICAL DATA (kJ mol^{-1}) FOR $W(\eta\text{-}C_5H_5)_2L_2$ COMPLEXES

Complex	ΔH_f^0 (c)	ΔH_s^0 ^{a}	ΔH_f^0 (g)	$\bar{D}$(W—L)	$\bar{E}$(W—L) ^{b}	Reference
$W(\eta\text{-}C_5H_5)_2Cl_2$ ^{c}	−71.1 ± 2.5	(104.6 ± 4.2)	33.5 ± 4.9	347.3 ± 0.8 ^{d}	347.3 ± 0.8	6
$W(\eta\text{-}C_5H_5)_2Br_2$	6.9 ± 17.7	(104.6 ± 4.2)	111.5 ± 18.2	299 ± 9	299 ± 9	11
$W(\eta\text{-}C_5H_5)_2I_2$	57.8 ± 7.6	(104.6 ± 4.2)	162.4 ± 8.7	268 ± 5	268 ± 5	2
$W(\eta\text{-}C_5H_5)_2H_2$	214.8 ± 5.0	96.2 ± 2.1	311.0 ± 5.4	305 ± 4	305 ± 4	9
$W(\eta\text{-}C_5H_5)_2(CH_3)_2$	284.8 ± 3.5	(74.6 ± 4.2)	359.4 ± 5.5	210 ± 3	181 ± 9	10, 12
$W(\eta\text{-}C_5H_5)_2(OCOC_6H_5)_2$	−448.9 ± 3.5	(98 ± 10)	−350.9 ± 10.6	342 ± 7	357 ± 10	1
$W(\eta\text{-}C_5H_5)_2(OCOCF_3)_2$	−1914.5 ± 3.8	(94 ± 10)	−1820.5 ± 10.7	337 ± 12	356 ± 10	1

^{a,b,c,d} See notes to Table 3.

TABLE 5

THERMOCHEMICAL DATA (kJ mol^{-1}) FOR $Ti(\eta\text{-}C_5H_5)_2L_2$ COMPLEXES

Complex	ΔH_f^0 (c)	ΔH_s^0 ^{a}	ΔH_f^0 (g)	$\bar{D}$(Ti—L)	$\bar{E}$(Ti—L) ^{b}	Reference
$Ti(\eta\text{-}C_5H_5)_2Cl_2$ ^{c}	−383.2 ± 7.5	118.8 ± 2.1	−264.4 ± 7.8	430.5 ± 1.3 ^{d}	430.5 ± 1.3	6
$Ti(\eta\text{-}C_5H_5)_2(C_6H_5)_2$	294.4 ± 8.8	(88 ± 8)	382.4 ± 11.9	311 ± 10	271 ± 9	33
$Ti(\eta\text{-}C_5H_5)_2(OCOC_6H_5)_2$	−775.2 ± 8.1	(112 ± 8)	−663.2 ± 11.4	432 ± 6	448 ± 9	1
$Ti(\eta\text{-}C_5H_5)_2(OCOCF_3)_2$	−2219.0 ± 8.0	108 ± 8	−2111.0 ± 11.3	417 ± 11	435 ± 9	1
$Ti(\eta\text{-}C_5H_5)_2(OCOCCl_3)_2$	−1062.8 ± 18.5	(130 ± 8)	−932.8 ± 20.2	430 ± 11	448 ± 9	33
$Ti(\eta\text{-}C_5H_5)_2(OC_6H_5)_2$	−379.2 ± 8.0	(97 ± 8)	−282.2 ± 11.3	366 ± 11	455 ± 9	This work
$Ti(\eta\text{-}C_5H_5)_2(OC_6H_4\text{-}2\text{-}CH_3)_2$	−416.7 ± 8.1	(104 ± 8)	−312.7 ± 11.4	349 ± 11	438 ± 9	This work
$Ti(\eta\text{-}C_5H_5)_2(OC_6H_4\text{-}3\text{-}CH_3)_2$	−393.6 ± 8.1	(104 ± 8)	−289.6 ± 11.4	334 ± 11	423 ± 9	This work
$Ti(\eta\text{-}C_5H_5)_2(OC_6H_4\text{-}4\text{-}CH_3)_2$	−416.5 ± 7.8	(104 ± 8)	−312.5 ± 11.2	352 ± 11	441 ± 9	This work
$Ti(\eta\text{-}C_5H_5)_2(OC_6H_4\text{-}2\text{-}Cl)_2$	−407.6 ± 21.5	(90 ± 10)	−317.6 ± 23.7	335 ± 12	424 ± 10	This work
$Ti(\eta\text{-}C_5H_5)_2(NC_8H_6)_2$	219.9 ± 12.0	(109 ± 10)	328.9 ± 15.6		329 ± 10	34

^{a,b,c,d} See notes to Table 3.

Several alternative methods were available for obtaining E(L—H): (1) Sanderson's method [24,25], (2) correlations between mean bond enthalpy terms and bond distances, and (3) use of Laidler parameters [26,27]. Sanderson's method, though it provides fairly accurate values in some cases, leads to large disagreement with experimental results in others. As far as curves of E versus r are concerned, since some of them are quite steep a small uncertainty in r causes large uncertainties in E. Laidler parameters were therefore preferred for deriving $\Delta H_f^0(\mathrm{L}^*,\mathrm{g})$ or E(L—H) values.

Some of the conclusions which can be drawn from the results in Tables 3, 4 and 5 have already been considered in earlier papers. Here we are mainly concerned with checking the "internal consistency" of the thermochemical data.

For the tungsten complexes, it was noticed before [11] that the assumption

$$\begin{aligned}\bar{D}(\mathrm{W{-}Cl}) &= \bar{E}(\mathrm{W{-}Cl}) \text{ in } \mathrm{WCl_6}\\ &= \bar{E}(\mathrm{W{-}Cl}) \text{ in } \mathrm{W(\eta\text{-}C_5H_5)_2Cl_2}\end{aligned}$$

was reasonable, since the value of $\bar{E}$(W—Br) in $\mathrm{WBr_6}$, 290 kJ $\mathrm{mol^{-1}}$, compares well with the mean value given in Table 4, which was evaluated through eq. 14 by use of the above assumption. Again, the value for $\bar{E}(\mathrm{W{-}OCH_3})$ * in $\mathrm{W(OCH_3)_6}$, ca. 381 kJ $\mathrm{mol^{-1}}$ [28], is not far from $\bar{E}$(W—O) presented in Table 4. It is must be noted, however, that $\bar{E}(\mathrm{W{-}CH_3})$ ** in $\mathrm{W(CH_3)_6}$, ca. 130 kJ $\mathrm{mol^{-1}}$ [29], is much lower than $\bar{E}(\mathrm{W{-}CH_3})$ in Table 4; it has been suggested that this difference is a consequence of steric strain in $\mathrm{W(CH_3)_6}$ [10].

$\bar{D}$(Ti—O) in $\mathrm{Ti(\eta\text{-}C_5H_5)_2(OR)_2}$ complexes (Table 5) varies from about 334 kJ $\mathrm{mol^{-1}}$ to 432 kJ $\mathrm{mol^{-1}}$, while $\bar{E}$(Ti—O) varies only from 423 kJ $\mathrm{mol^{-1}}$ to 455 kJ $\mathrm{mol^{-1}}$, reflecting that the phenoxy radicals OPh are stabilized more by resonance than are OR alkoxy radicals. The average value of those $\bar{E}$(Ti—O), ca. 439 kJ $\mathrm{mol^{-1}}$, is not far from an average $\bar{E}$(Ti—O) ~460 kJ $\mathrm{mol^{-1}}$ in $\mathrm{Ti(OR)_4}$ compounds (R = $\mathrm{C_2H_5}$, n-$\mathrm{C_3H_7}$, i-$\mathrm{C_3H_7}$, and t-$\mathrm{C_4H_9}$; $ER(\mathrm{OR}^*)$ was taken as —23 kJ $\mathrm{mol^{-1}}$) [30]. For the complex $\mathrm{Ti(\eta\text{-}C_5H_5)_2(NC_8H_6)_2}$ $\bar{E}$(Ti—N) is in good agreement with $\bar{E}$(Ti—N) ~339 kJ $\mathrm{mol^{-1}}$ in $\mathrm{Ti(NR_2)_4}$ (R = $\mathrm{CH_3}$ and $\mathrm{C_2H_5}$) [31].

Mean bond-enthalpy terms are certainly more useful in discussing bond strengths than mean bond-disruption enthalpies, particularly if one wishes to correlate these bond strengths with structural data. As $\bar{D}$ values contain the energetics of the transformations undergone by the fragments, they should be used only for consideration of reaction data, unless, of course, the reorganization enthalpies of a series of ligands are significantly constant so that the pattern does not change in going from $\bar{E}$ to $\bar{D}$.

Acknowledgements

Thanks are due to the Junta Nacional de Investigação Científica e Tecnológica and to the Instituto Nacional de Investigação Científica for financing this work. M.S.S. thanks L.N.E.T.I. for granting him leave of absence to participate in this project.

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* $ER(\mathrm{OCH_3^*}) \sim -23$ kJ $\mathrm{mol^{-1}}$.

** $ER(\mathrm{CH_3^*}) \sim 29$ kJ $\mathrm{mol^{-1}}$.

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