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Estimation of standard enthalpies of formation of inorganic and organometallic compounds. II

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Abstract

Correlations between the standard enthalpies of formation of organometallic and inorganic compounds MX_nL_m and of ligands LH or LH_m, both in their standard reference states, are examined in detail and illustrated with examples. They provide a simple method of predicting new values and assessing experimental data.

Introduction

A simple method for estimating standard enthalpies of formation of crystalline inorganic and organometallic complexes, MX_nL_m, was described in an earlier paper [1]. It involves linear correlations between $\Delta H_f^0(MX_nL_m, c)$ and the standard enthalpies of formation of ligands L or LH in their standard reference states (rs), i.e. their stable physical states at 298.15 K and 1 bar. Application of the method to several types of complexes [1] has demonstrated its value, but also raised a number of interesting questions related to the physical meaning of the linear correlations. Since a better understanding of these correlations is essential for their correct use, we decided to reexamine the approach and to test its application to other families of compounds involving metal–carbon or metal–oxygen bonds, namely ML_2 and ML_3, where M are metals from groups 12 and 13; $M(OR)_n$, where M = Ti, Nb, Ta and R = alkyl; $ThCp^*_2L_2$, $ThCp^*_2(OBu\text{-}t)L$, $ThCp^*_2L$, and $UCp^*_2L_2$, where $Cp^* = \eta^5\text{-}C_5Me_5$. Some correlations described earlier [1] have also been reexamined by use of the results of recent thermochemical studies. Data for the standard enthalpies of formation of ligands were taken from Sussex-N.P.L. Tables [2], except for those for $SiMe_4$ [3].

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The linear correlations

Consider a series of molecules MX_nL_m, with a constant moiety MX_n, in which L are monodentate ligands bonded to the metal atom. The linear correlations between $\Delta H_f^0(MX_nL_m, rs)$ and $\Delta H_f^0(LH, rs)$ are shown in Fig. 1 for this general case [4*]. Three parallel lines are drawn, each of them defining a "family" of ligands. For example, lines A, B, C could involve ligands bonded to the metal through carbon, oxygen, and halogen atoms, respectively. Such a pattern has been observed, for example for the complexes $TiCp_2L_2$ ($Cp = \eta^5\text{-}C_5H_5$) [1].

The implications of the linear plots can be analysed by considering the enthalpy balance of any reaction involving both the molecules MX_nL_m and LH. In our previous paper we arbitrarily chose reaction 1.

$$MX_nL_m(rs) + mHCl(g) = MX_nCl_m(rs) + mLH(rs) \quad (1)$$

Since a given family of ligands is described by the linear eq. 2, a comparison between this equation and the enthalpy balance for reaction 1, $\Delta H^0(1)$, eq. 3, leads to the conclusion that $\Delta H^0(1)$ is constant for that series of ligands L.

$$\Delta H_f^0(MX_nL_m, rs) = a\Delta H_f^0(LH, rs) + b \quad (2)$$

$$\Delta H_f^0(MX_nL_m, rs) = m\Delta H_f^0(LH, rs) - \Delta H^0(1) + \Delta H_f^0(MX_nCl_m, rs) - m\Delta H_f^0(HCl, g) \quad (3)$$

As shown previously [1], the slope of the linear plot reflects the number of ligands L bonded to the metal atom ($m = a$). It can be the same for ligands from different

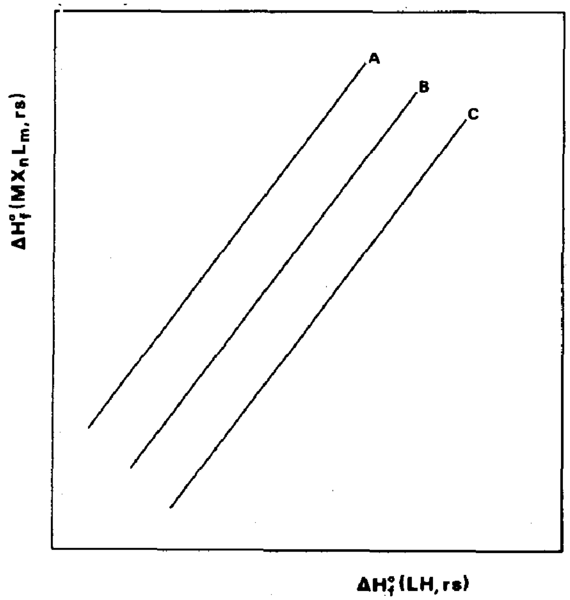

Fig. 1. General representation of the correlation between $\Delta H_f^0(MX_nL_m, rs)$ and $\Delta H_f^0(LH, rs)$. The parallel lines define different "families" of ligands, and the slope reflects the number of ligands L bonded to the metal M (see text).

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

families, as shown in Fig. 1. A particular family is characterized by the intercept (b, eq. 2), this being determined by $\Delta H^0(1)$, since $\Delta H_f^0(\mathrm{MX}_n\mathrm{Cl}_m, \mathrm{rs}) - m\Delta H_f^0(\mathrm{HCl, g})$ is constant for the three families in Fig. 1.

The constancy of $\Delta H^0(1)$ has been discussed before [1] but is summarized here for sake of clarity. Scheme 1 relates $\Delta H^0(1)$ to the enthalpy change of the same reaction with reactants and products in the gas phase (ΔH^0_{V1}, ΔH^0_{V2}, and ΔH^0_{V3} are vaporization or sublimation-enthalpies). This enables $\Delta H^0(1)$ to be defined in terms of bond dissociation enthalpies, eq. 4.

$$\begin{tikzcd}
\mathrm{MX}_n\mathrm{L}_m(\mathrm{rs}) \arrow[d, "\Delta H^0_{\mathrm{V1}}"] & + & m\mathrm{HCl(g)} \arrow[d, "0"] & = & \mathrm{MX}_n\mathrm{Cl}_m(\mathrm{rs}) \arrow[d, "\Delta H^0_{\mathrm{V2}}"] & + & m\mathrm{LH(rs)} \arrow[d, "m\Delta H^0_{\mathrm{V3}}"] \\
\mathrm{MX}_n\mathrm{L}_m(\mathrm{g}) & + & m\mathrm{HCl(g)} & = & \mathrm{MX}_n\mathrm{Cl}_m(\mathrm{g}) & + & m\mathrm{LH(g)}
\end{tikzcd}$$

Scheme 1

$$\Delta H^0(1) = m[\bar{D}(\mathrm{M{-}L}) - D(\mathrm{L{-}H})] + [\Delta H^0_{\mathrm{V1}} - m\Delta H^0_{\mathrm{V3}}] + [mD(\mathrm{H{-}Cl}) - m\bar{D}(\mathrm{M{-}Cl}) - \Delta H^0_{\mathrm{V2}}] \quad (4)$$

Since the third term in eq. 4, $[mD(\mathrm{H{-}Cl}) - m\bar{D}(\mathrm{M{-}Cl}) - \Delta H^0_{\mathrm{V2}}]$, is constant for the three families of ligands in Fig. 1, we conclude that $\Delta H^0(1)$ for each family is determined by the first two terms. Although experimental data for sublimation enthalpies of complexes are rather scarce, we have suggested [1] that the constancy of $\Delta H^0(1)$ for a family may be due to a compensation between the intra- and the inter-molecular terms in eq. 4. This idea is supported by some of the examples below, since the plot $\Delta H_f^0(\mathrm{MX}_n\mathrm{L}_m, \mathrm{rs})$ against $\Delta H_f^0(\mathrm{LH, rs})$ is better than that of $\Delta H_f^0(\mathrm{MX}_n\mathrm{L}_m, \mathrm{g})$ against $\Delta H_f^0(\mathrm{LH, g})$. However, the fact that the correlation holds for the gas state implies that the intramolecular compensation is much more important than the intermolecular term: the constancy of $\Delta H^0(1)$ is mainly determined by the difference $\bar{D}(\mathrm{M{-}L}) - D(\mathrm{L{-}H})$. In other words, the correlations are observed whenever metal–ligand bond dissociation enthalpies parallel ligand–hydrogen bond dissociation enthalpies. Different families yield different values for $\bar{D}(\mathrm{M{-}L}) - D(\mathrm{L{-}H})$, and this leads to different intercepts.

The above discussion is also valid for complexes with polydentate ligands. For example, in complexes of the type $\mathrm{MX}_n\mathrm{L}$, where L is a bidentate ligand, eqs. 1 and 4 transform into eqs. 5 and 6, respectively.

$$\mathrm{MX}_n\mathrm{L(rs)} + m\mathrm{HCl(g)} = \mathrm{MX}_n\mathrm{Cl}_m(\mathrm{rs}) + \mathrm{LH}_m(\mathrm{rs}) \quad (5)$$

$$\Delta H^0(5) = [D(\mathrm{M{-}L}) - m\bar{D}(\mathrm{L{-}H})] + [\Delta H^0_{\mathrm{V1}} - \Delta H^0_{\mathrm{V3}}] + [mD(\mathrm{H{-}Cl}) - m\bar{D}(\mathrm{M{-}Cl}) - \Delta H^0_{\mathrm{V2}}] \quad (6)$$

A linear correlation (slope 1) for a series of ligands L will therefore be observed if the difference $D(\mathrm{M{-}L}) - m\bar{D}(\mathrm{L{-}H})$ is constant. As in the case of monodentate ligands, the value of this constant characterizes the family.

An important question about the use of the correlations concerns the distinction between anionic and neutral ligands. As illustrated below for the complexes $\mathrm{MoCp_2L}$, the former group includes $\mathrm{SO_4}^{2-}$, $\mathrm{C_6H_4O_2}^{2-}$ (catecholate), etc., and the latter includes C_2H_4, C_2Ph_2, and azobenzene. Should we plot $\Delta H_f^0(\mathrm{MoCp_2L}, \mathrm{c})$ against $\Delta H_f^0(\mathrm{LH}_m, \mathrm{rs})$ for all these ligands or should we use $\Delta H_f^0(\mathrm{L}, \mathrm{rs})$ for the neutral ligands?

In our early paper [1] the use of $\Delta H_f^0(\mathrm{L}, \mathrm{rs})$ for azobenzene led to a good fit to the line defined by the remaining points for the anionic ligands. In addition, a preliminary value of $\Delta H_f^0[\mathrm{MoCp_2(C_2H_4)}, \mathrm{c}]$ was also fitted by use of $\Delta H_f^0(\mathrm{C_2H_4}, \mathrm{g})$. The consequences of this option will now be examined by the method described above. Reaction 7 is equivalent to reaction 5, but involves the formation of the free ligand L. It leads to eq. 8, which reveals that metal–ligand bond dissociation enthalpies are not compensated by ligand–hydrogen bond dissociation enthalpies (ΔH_{V3}^0 is now the vaporization or sublimation enthalpy of L).

$$\mathrm{MX}_n\mathrm{L(rs)} + m\mathrm{HCl(g)} = \mathrm{MX}_n\mathrm{Cl}_m\mathrm{(rs)} + \mathrm{L(rs)} + \frac{m}{2}\mathrm{H_2(g)} \tag{7}$$

$$\Delta H^0(7) = [D(\mathrm{M{-}L})] + [\Delta H_{V1}^0 - \Delta H_{V3}^0] + [mD(\mathrm{H{-}Cl}) - m\bar{D}(\mathrm{M{-}Cl}) - mD(\mathrm{H{-}H})/2 - \Delta H_{V2}^0] \tag{8}$$

The existence of a unique correlation involving both the neutral (C_2H_4, *trans*-N_2Ph_2) and the anionic ligands (SO_4^{2-}, etc.) would imply that $\Delta H^0(5) = \Delta H^0(7) =$ constant ($m = 2$) for the series of ligands. The fact that the correlation is observed must be due to fortuitous cancellation of terms in eqs. 6 and 8. For instance, in eq. 8, the metal–ethylene bond is weaker than the metal–azobenzene bond but this is compensated by a larger difference in the intermolecular term, so that $[D(\mathrm{M{-}L})] + [\Delta H_{V1}^0 - \Delta H_{V3}^0]$ is nearly constant (~ 137 and ~ 126 kJ $\mathrm{mol^{-1}}$ for C_2H_4 and *trans*-N_2Ph_2, respectively). As illustrated below (Example 1), the compensation may not necessarily hold for other ligands. The fortuitous character of the above correlation is also suggested by its lack of physical meaning. Why should bidentate ligands involving metal–carbon, metal–nitrogen, and metal–oxygen bonds behave differently from monodentate ligands, i.e. belong to one family? In conclusion, we believe that neutral and anionic ligands must be handled identically: the enthalpy of formation of the complex is plotted against $\Delta H_f^0(\mathrm{LH_m}, \mathrm{rs})$ and not $\Delta H_f^0(\mathrm{L}, \mathrm{rs})$.

While the previous conclusion does not raise any practical problems for ligands such as C_2H_4 and *trans*-N_2Ph_2 (the enthalpies of formation of C_2H_6 and $N_2Ph_2H_2$ are tabulated), there are many cases where the lack of experimental data for the hydrogenated ligands may prevent accurate correlation. Typical examples appear in reference 1, and the plots involving arene-chromium complexes, CrL_2 and $Cr(CO)_3L$, and adducts $MX_2 \cdot n\mathrm{L}$ (M = Zn, Cd, Hg; X = halogen; L = oxygen donor). In these cases there is no alternative to use of $\Delta H_f^0(\mathrm{L}, \mathrm{rs})$. A correlation is observed (i.e. eq. 8 holds) because $D(\mathrm{M{-}L})$ or $[D(\mathrm{M{-}L})] + [\Delta H_{V1}^0 - \Delta H_{V3}^0]$ are fairly constant for each series of ligands [5].

Example 1: MCp_2L_n complexes

The standard enthalpies of formation of the crystalline complexes $MoCp_2Et_2$ and $MoCp_2(n\text{-}Bu)_2$ have been determined recently [6]. The results are included in Fig. 2, and enabled definition of correlation for the family of molybdenum–carbon σ-bonds (eq. 9). The other line, eq. 10, involving molybdenum–oxygen and -sulfur bonds, was defined previously [1].

$$\Delta H_f^0(\mathrm{MoCp_2L_2}, \mathrm{c}) = (2.150 \pm 0.441)\ \Delta H_f^0(\mathrm{LH}, \mathrm{rs}) + (411.7 \pm 43.1) \tag{9}$$

$$\Delta H_f^0(\mathrm{MoCp_2L_2}, \mathrm{c}) = (2.011 \pm 0.041)\ \Delta H_f^0(\mathrm{LH}, \mathrm{rs}) + (194.2 \pm 16.4) \tag{10}$$

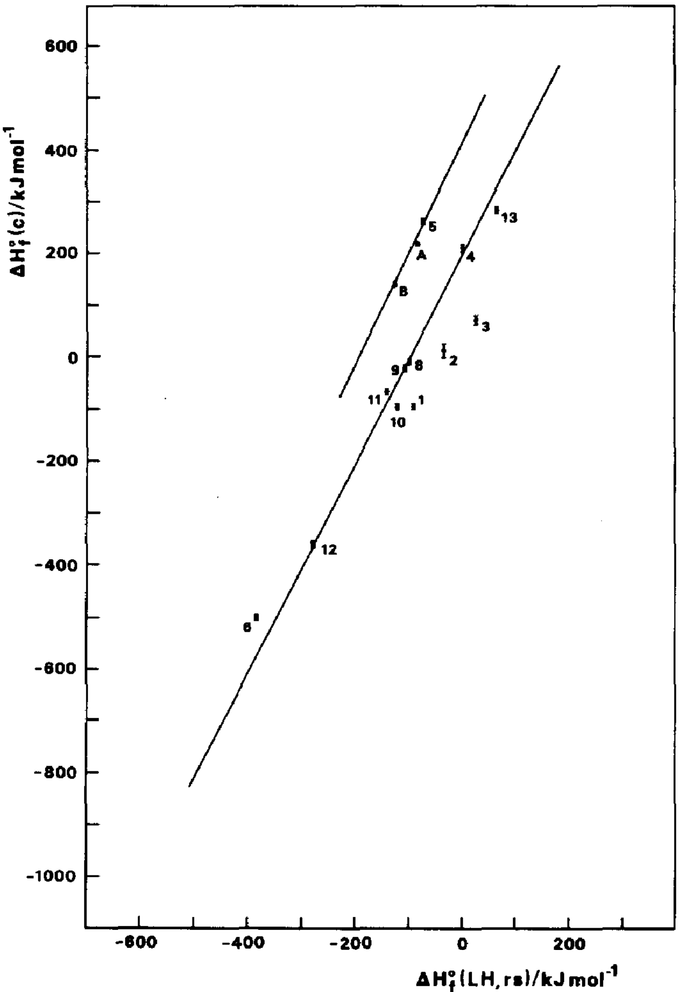

Fig. 2. $\Delta H_f^0(\text{MoCp}_2\text{L}_2, \text{c})$ vs. $\Delta H_f^0(\text{LH, rs})$. Point numbers correspond to the following ligands: 1 = Cl, 2 = Br, 3 = I, 4 = H, 5 = Me, 6 = PhCOO, 7 = CF_3COO (not shown in the figure), 8 = n-PrS, 9 = i-PrS, 10 = n-BuS, 11 = t-BuS, 12 = n-$\text{C}_{10}\text{H}_{21}\text{S}$, 13 = PhS, A = Et, B = n-Bu.

Although eq. 9 was obtained with only three points and thus must be used with some caution, it allows us to predict enthalpies of formation of other analogous complexes containing molybdenum–carbon σ-bonds. The uncertainty in the estimates will of course, be reduced when more data become available but it is, noteworthy that the difference between the intercepts of eqs. 9 and 10, 218 kJ mol^{-1}, is close to the value obtained from the two equivalent correlations defined for TiCp_2L_2 compounds, namely 205 kJ mol^{-1} [1]. If the intermolecular terms in eq. 4 are neglected, the above differences are given by eqs. 11 and 12, where R represents a ligand σ-bonded to the metal through a carbon atom and L represents an oxygen or sulfur ligand.

$$2[\bar{D}(\text{Mo–R}) - \bar{D}(\text{Mo–L})] + 2[D(\text{L–H}) - D(\text{R–H})] = 218 \qquad (11)$$

$$2[\bar{D}(\text{Ti–R}) - \bar{D}(\text{Ti–L})] + 2[D(\text{L–H}) - D(\text{R–H})] = 205 \qquad (12)$$

By subtracting these two equations we conclude that mean bond dissociation enthalpy differences $\bar{D}(\text{M–R}) - \bar{D}(\text{M–L})$ are in the same range for the molybdenum and the titanium complexes. For example, $\bar{D}$(Mo–Me) – $\bar{D}$(Mo–O_2CCF_3) ~ –150 kJ mol^{-1} and $\bar{D}$(Ti–Me) – $\bar{D}$(Ti–O_2CCF_3) ~ –135 kJ mol^{-1} [7]. Although this comparison is approximate, since the intermolecular terms have been neglected in the discussion, it emphasizes that differences between families (or between the intercepts) can be nearly identical for several metals, this being mainly a consequence of similar bond enthalpy differences. In other words, the correlations for $MoCp_2L_2$ and $TiCp_2L_2$ complexes can be superimposed by using a scale factor. The same conclusion seems to hold for the analogous tungsten compounds: the only available value for the family involving tungsten–carbon σ-bonds relates to WCp_2Me_2 [1] and can be used together with the linear correlation for the oxygen and sulfur ligands to estimate the constant for an equation equivalent to 11 or 12. The obtained value, 192 kJ mol^{-1}, is close to that for the titanium complexes, which is probably more reliable than that in eq. 11 because it was derived from a larger number of data.

The correlation for $MoCp_2L$ complexes, where L are bidentate ligands, was redefined in accord with the discussion above, i.e. ΔH_f^0($MoCp_2L$, rs) was plotted against ΔH_f^0(LH_2, rs) and not against ΔH_f^0(L, rs). Three distinct families are now apparent in Fig. 3, involving respectively metal–oxygen, metal–nitrogen, and metal–carbon bonds. The linear correlation for the oxygen ligands is given by eq. 13.

$$\Delta H_f^0(\mathrm{MoCp_2L, c}) = (1.124 \pm 0.010)\Delta H_f^0(\mathrm{LH_2, rs}) + (264.5 \pm 5.0) \qquad (13)$$

Unfortunately, there is only one experimental value for nitrogen ligands and two for carbon ligands. Note, however, that these two points are fitted by a line parallel to that defined by eq. 13, which suggests that they define a family for Mo–C bonds.

Although more experimental data are needed in order to confirm the correlation for carbon bidentate ligands, this matter can be further explored by using thermochemical values for other similar organometallic molecules. Reaction-solution calorimetric results on two thorium complexes, $ThCp_2^{\star}(C_4H_6)$ and $ThCp_2^{\star}(CH_2CMeCMeCH_2)$ [8], can be used to derive their relative enthalpies of formation, i.e. $\Delta H_f^0(\mathrm{ThCp_2^{\star}L, c}) - Y$, where $Y = \Delta H_f^0[\mathrm{ThCp_2^{\star}(OBu\text{-}t)_2, c}] - 2\Delta H_f^0(\mathrm{t\text{-}BuOH, l})$. When these values, 216.4 ± 13.6 and 145.9 ± 14.8 kJ mol^{-1}, respectively, are plotted against the enthalpies of formation of *trans*-2-butene (gas) and 2,3-dimethyl-2-butene (liquid), the observed slope, 0.8, is slightly smaller than was expected (slope 1), but may be affected by the uncertainties in each value.

The above thorium complexes can, in fact, be expected to belong to the same family, but the question arises of whether the enthalpies of formation of complexes $ThCp_2^{\star}(C_2H_4)$ and $ThCp_2^{\star}(C_2Ph_2)$ would also be fitted by the same correlation, or, alternatively, whether the enthalpies of formation of $MoCp_2(C_4H_6)$ and $MoCp_2(CH_2CMeCMeCH_2)$ can be predicted by the plot involving the two above $MoCp_2L$ complexes. In short, do the ligands C_2H_4, C_2Ph_2, C_4H_6, and $CH_2CMeCMeCH_2$ belong to the same family? As stated above, confident answer to this question must await more experimental data for metallacycles and metal–olefin complexes. However, it is of interest to compare the enthalpy of reaction 14 for the molybdenum and thorium complexes under discussion. The results are displayed in Table 1, and it can be seen that ΔH^0(14) is nearly constant, particularly if the uncertainties are considered [9*]. It should be noted that reaction 14 is just another arbitrary reaction for analysis of the linear correlations; it involves both the

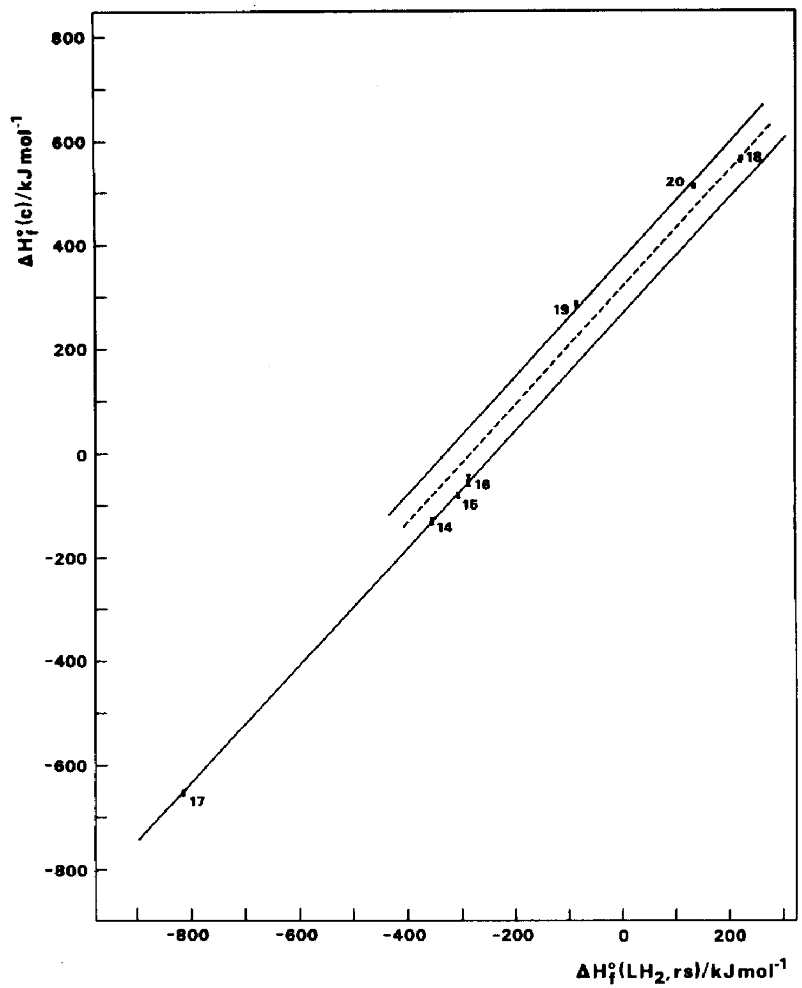

Fig. 3. $\Delta H_f^0(MoCp_2L, c)$ vs. $\Delta H_f^0(LH_2, rs)$. Point numbers correspond to the following ligands: 14 = $C_6H_4O_2$, 15 = $C_{10}H_6O_2$, 16 = $C_{14}H_8O_2$, 17 = SO_4, 18 = N_2Ph_2, 19 = C_2H_4, 20 = C_2Ph_2.

complex MCp'_2L ($Cp' = Cp$ or $Cp^\star$) and LH_2, and it was chosen as an alternative to reaction 5 because the enthalpy of formation of $ThCp^\star_2Cl_2$ is unknown but $\Delta H_f^0(MCp'Me_2, c)$ is available for M = Mo and Th (in this case, a relative value, 141.0 ± 6.8 kJ mol^{-1}, was derived from calorimetric data [8]).

$$MCp'_2L(c) + 2CH_4(g) = MCp'_2Me_2(c) + LH_2(rs) \qquad (14)$$

Table 1

$\Delta H^0(14)$ for several molybdenum and thorium complexes (kJ mol^{-1})

MCp'_2L	LH_2	$\Delta H^0(14)$
$MoCp_2(C_2H_4)$	C_2H_6	42.4 ± 9.2
$MoCp_2(C_2Ph_2)$	*trans*-$C_2H_2Ph_2$	35.7 ± 9.6
$ThCp^\star_2(C_4H_6)$	2-C_4H_8	61.4 ± 15.2 [a]
$ThCp^\star_2(CH_2CMeCMeCH_2)$	C_2Me_4	42.1 ± 16.3

[a] See note 9.

If the "constancy" of $\Delta H^0(14)$ is accepted, it follows that the four ligands belong to the same family. In addition, a simple analysis in terms of bond dissociation enthalpies (neglecting intermolecular contributions), shows that it also implies that $D(\mathrm{Mo{-}L}) - 2\bar{D}(\mathrm{Mo{-}Me})$ is approximately equal to $D(\mathrm{Th{-}L}) - 2\bar{D}(\mathrm{Th{-}Me})$, which in turn indicates that differences between families may be similar for the molybdenum and thorium complexes (see the above discussion for Ti, Mo, and W complexes).

A larger set of experimental values will allow a more detailed discussion of the preceding conclusions, which, at this stage, are rather speculative. If they are confirmed, or if our ability to assign a ligand to a given family improves, it will be possible to predict the enthalpies of formation of complexes with a variety of bidentate ligands.

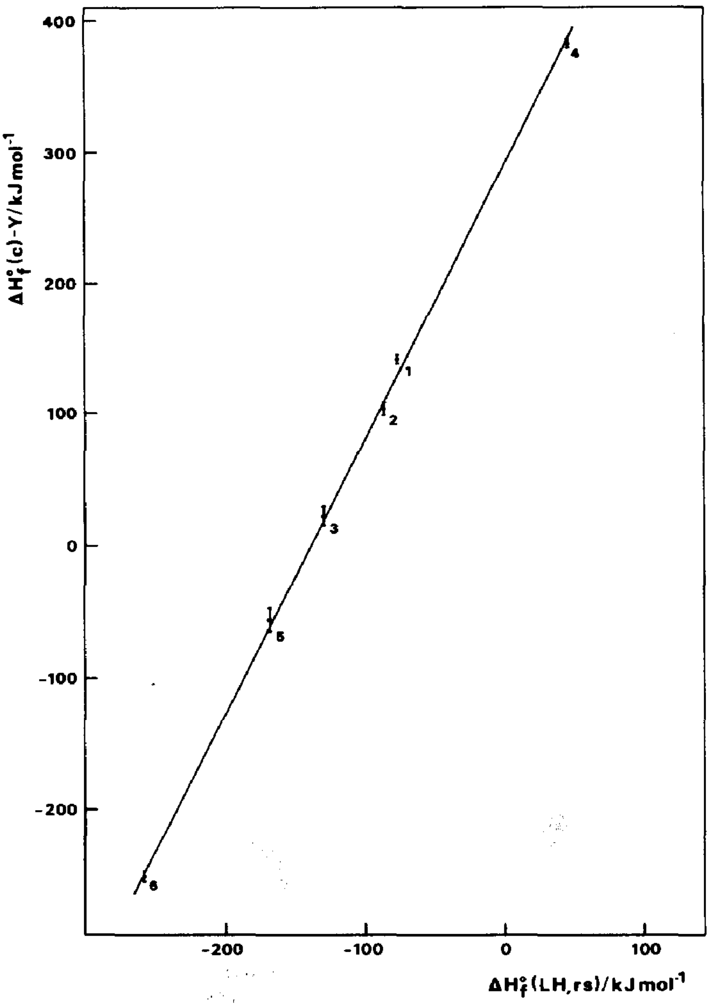

Fig. 4. Relative values of $\Delta H_f^0(\mathrm{ThCp}_2^\star L_2, c)$ vs. $\Delta H_f^0(\mathrm{LH, rs})$. Point numbers correspond to the following ligands: 1 = Me, 2 = Et, 3 = n-Bu, 4 = Ph, 5 = CH_2CMe_3, 6 = CH_2SiMe_3. $Y = \Delta H_f^0[\mathrm{ThCp}_2^\star(\mathrm{OBu\text{-}t})_2, c] - 2\Delta H_f(\mathrm{t\text{-}BuOH, l})$.

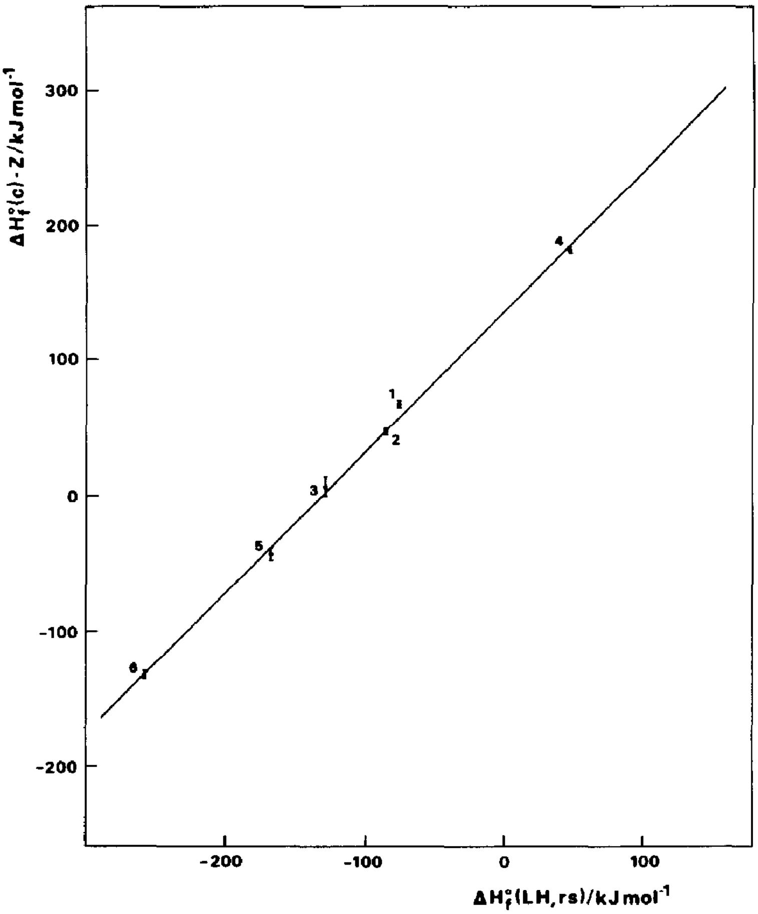

Fig. 5. Relative values of ΔH_f^0[ThCp$_2^\star$(OBu-t)L, c] vs. ΔH_f^0(LH, rs). Point numbers correspond to the following ligands: 1 = Me, 2 = Et, 3 = n-Bu, 4 = Ph, 5 = CH_2CMe_3, 6 = CH_2SiMe_3. $Z = \Delta H_f^0$[ThCp$_2^\star$(OBu-t)$_2$, c] $- \Delta H_f$(t-BuOH, l).

The application of the linear correlation to thorium complexes is illustrated in Fig. 4 and 5 for ThCp$_2^\star$L$_2$ (eq. 15) and ThCp$_2^\star$(OBu-t)L (eq. 16) molecules. Their enthalpies of formation were also derived from calorimetric data [8], and are relative to $Y = \Delta H_f^0$[ThCp$_2^\star$(OBu-t)$_2$, c] $- 2\Delta H_f^0$(t-BuOH, l) or $Z = \Delta H_f^0$[ThCp$_2^\star$(OBu-t)$_2$, c] $- \Delta H_f^0$(t-BuOH, l), respectively. The fits are excellent (r = 0.9996 and 0.9990), with the expected slopes, and, as discussed above, imply that Th–L and L–H bond dissociation enthalpies follow nearly parallel trends. Surprisingly, however, the point for L = CH_2CMe_3 is fitted by eq. 15, although the neutron diffraction molecular structure of the complex ThCp$_2^\star$(CH_2CMe_3)$_2$ shows that one of the neopentyl moieties is subject to considerable steric effects [10]. The fact that an unusually high enthalpy of formation is not observed (see discussion below for the titanium alkoxides) suggests that in this case the steric strain is not reflected in the energetics, i.e. the distortion of the ligand is compensated in some way.

$$\Delta H_f^0(\mathrm{ThCp_2^\star L_2, c}) - Y = (2.070 \pm 0.031)\Delta H_f^0(\mathrm{LH, rs}) + (284.9 \pm 4.4) \qquad (15)$$

$$\Delta H_f^0[\mathrm{ThCp_2^\star(OBu\text{-}t)L, c}) - Z = (1.033 \pm 0.023)\Delta \mathrm{H}_f^0(\mathrm{LH, rs}) + (134.8 \pm 3.3) \qquad (16)$$

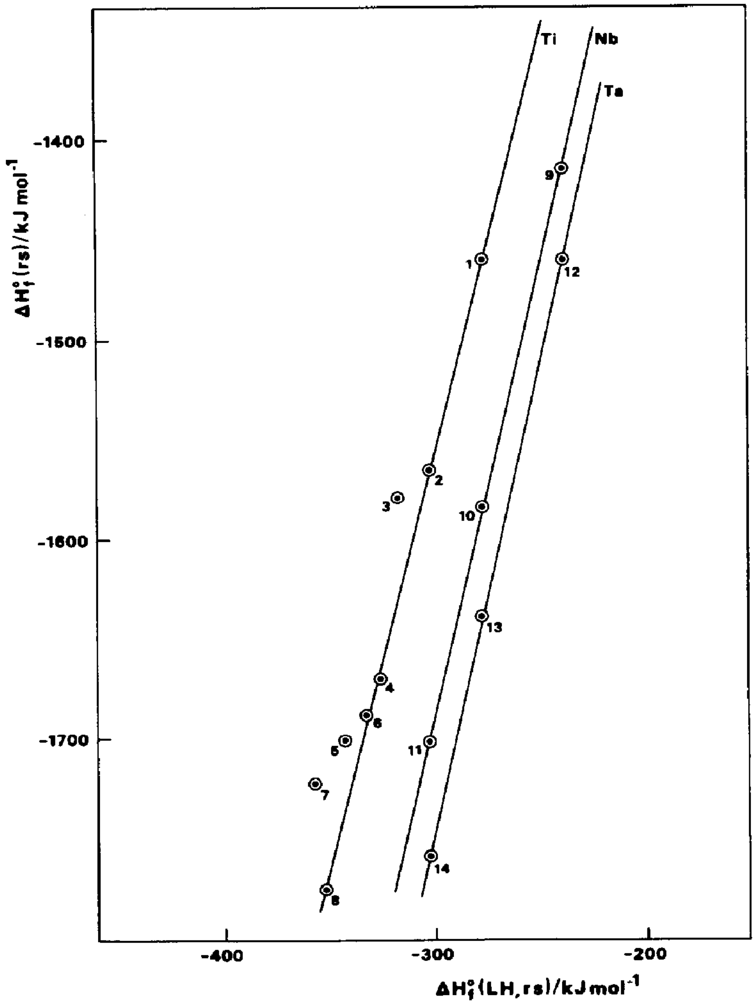

Fig. 6. $\Delta H_f^0[\mathrm{M(OR)}_n, \mathrm{rs}]$ vs. $\Delta H_f^0(\mathrm{ROH, rs})$ for M = Ti, Nb, and Ta. Point numbers correspond to the following R: 1 = Et, 2 = n-Pr, 3 = i-Pr, 4 = n-Bu, 5 = s-Bu, 6 = i-Bu, 7 = t-Bu, 8 = n-Pe, 9 = Me, 10 = Et, 11 = n-Pr, 12 = Me, 13 = Et, 14 = n-Pr.

The correlation obtained for the analogous uranium complexes, $\mathrm{UCp}_2^{\star}\mathrm{L}_2$, eq. 17 (r = 0.9988), was also obtained by deriving the relative enthalpies of formation of the complexes from reaction-solution calorimetric data [8]. Only three points are available, L = Me, $\mathrm{CH_2Ph}$, and $\mathrm{CH_2SiMe_3}$, corresponding respectively to $\Delta H_f^0(\mathrm{UCp}_2^{\star}\mathrm{L}_2, \mathrm{c}) - Y = 152.4 \pm 20.7$, 308.7 ± 14.8, and -259.1 ± 10.5 kJ mol^{-1}; $Y = \Delta H_f^0[\mathrm{UCp}_2^{\star}(\mathrm{OBu\text{-}t})_2, \mathrm{c}] - 2\Delta H_f^0(\mathrm{t\text{-}BuOH, l})$.

$$\Delta H_f^0(\mathrm{UCp}_2^{\star}\mathrm{L}_2, \mathrm{c}) - Y = (2.125 \pm 0.106)\Delta H_f^0(\mathrm{LH, rs}) + (294.2 \pm 16.4) \qquad (17)$$

Example 2: M(OR)$_n$ molecules

Figure 6 illustrates the application of the method for alkoxides of titanium, niobium, and tantalum. The enthalpies of formation of $\mathrm{Ti(OR)_4}$ were obtained by reaction-solution calorimetry [11], while the enthalpies of formation of $\mathrm{Nb(OR)_5}$ and $\mathrm{Ta(OR)_5}$ were measured by static bomb combustion calorimetry [12]. Although the lines for the two last series of compounds were defined from three points, they both are excellent, as demonstrated by the low values of the uncertainties in the slopes and the intercepts of eqs. 18 and 19.

$$\Delta H_f^0[\mathrm{Nb(OR)_5, rs}] = (4.522 \pm 0.030)\Delta H_f^0(\mathrm{ROH, rs}) - (332.2 \pm 8.1) \tag{18}$$

$$\Delta H_f^0[\mathrm{Ta(OR)_5, rs}] = (4.717 \pm 0.003)\Delta H_f^0(\mathrm{ROH, rs}) - (332.4 \pm 0.7) \tag{19}$$

The fit for $Ti(OR)_4$ compounds, eq. 20, deserves some attention. It was obtained by considering the values for n-alkyl ligands only, since the data for molecules containing branched alkyls can be affected by steric effects. This is, indeed, suggested by the fact that all the points for these ligands lie above the line in Fig. 6. The "excess" in the enthalpy of formation increases as expected, e.g. t-BuO > i-PrO > i-BuO, suggesting another possible application of the method, namely in quantification of the influence of steric constraints on the energetics of a molecule.

$$\Delta H_f^0[\mathrm{Ti(OR)_4, l}] = (4.138 \pm 0.023)\Delta H_f^0(\mathrm{ROH, rs}) - (313.5 \pm 7.1) \tag{20}$$

The availability of more experimental values for homoleptic compounds will permit checking of the above conclusion. For example, it would be of interest to measure the enthalpies of formation of alkoxides of zirconium and hafnium in order

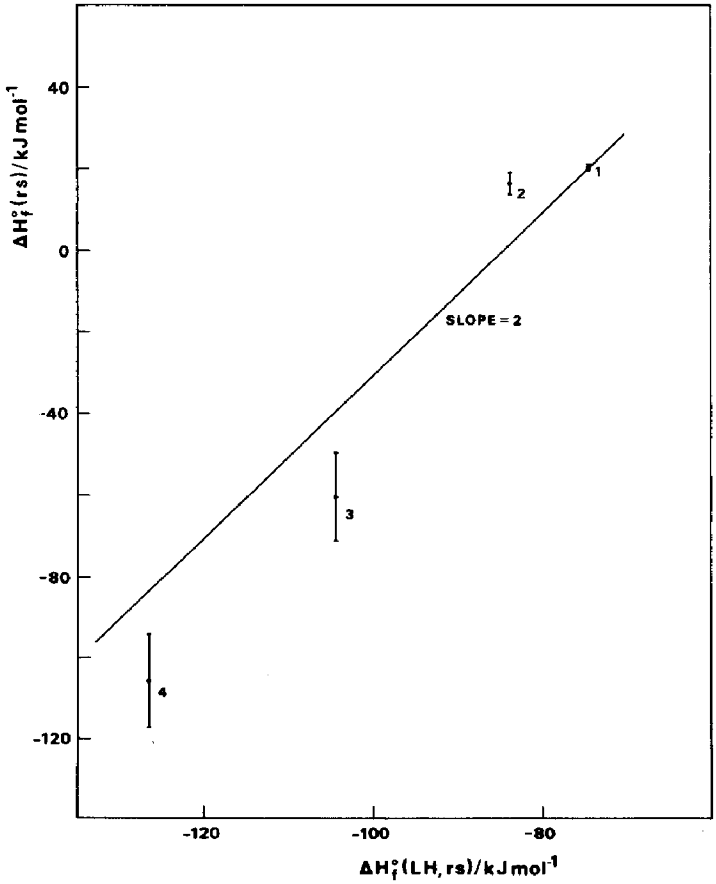

Fig. 7. $\Delta H_f^0[\mathrm{ZnL_2, rs}]$ vs. $\Delta H_f^0(\mathrm{LH, rs})$. Point numbers correspond to the following ligands: 1 = Me, 2 = Et, 3 = n-Pr, 4 = n-Bu. The line has slope 2 and was drawn from the point for L = Me.

to investigate whether the excesses in the enthalpies of formation in these cases are smaller than those for the corresponding titanium alkoxides.

Another feature that requires additional information relates to the slopes in eqs. 18 and 19. The fact that they are both < 5 may reflect the limitations of a three point linear regression, but perhaps arises from the dimerization of the molecules [13].

Example 3: ML_n molecules

The method of the linear correlations can be used to assess the validity of experimental data in cases in which the definition of a family is not uncertain. This happens, for instance, with the zinc alkyls, ZnR_2. The plot involving selected values

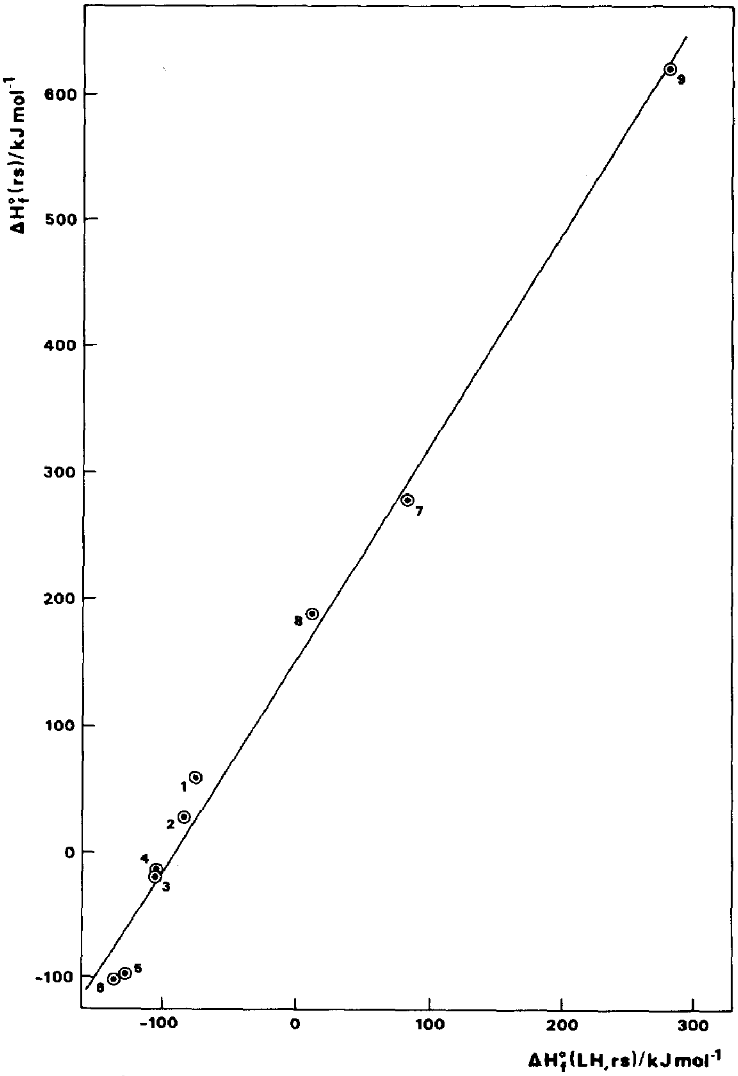

Fig. 8. $\Delta H_f^0[HgL_2, rs]$ vs. $\Delta H_f^0(LH, rs)$. Point numbers correspond to the following ligands: 1 = Me, 2 = Et, 3 = n-Pr, 4 = i-Pr, 5 = n-Bu, 6 = i-Bu, 7 = Ph, 8 = CH_2Ph, 9 = CCPh.

for the enthalpies of formation of these molecules [14] shows (Fig. 7) some scatter, which indicates some inconsistency in the data. The points for Me and Et come from reaction-solution measurements, whereas those for n-Pr and n-Bu came from static bomb experiments. It is well known that thermochemical study of these substances by static bomb combustion calorimetry is difficult [15]. In Fig. 7 we have arbitrarily drawn a line of slope 2 through the point for Me. This line seems to indicate that the values for Me and Et are slightly inconsistent, the difference between the enthalpies of formation of $ZnMe_2$ and $ZnEt_2$ should be higher than observed.

The equivalent data for mercury alkyls [2,14,16] (Fig. 8) are difficult to analyse, since no substantial scatter of data points was expected. Points 1–4 rely on reaction-solution calorimetry and the remaining values are based on static bomb combustion experiments, a technique that is considered more reliable for these

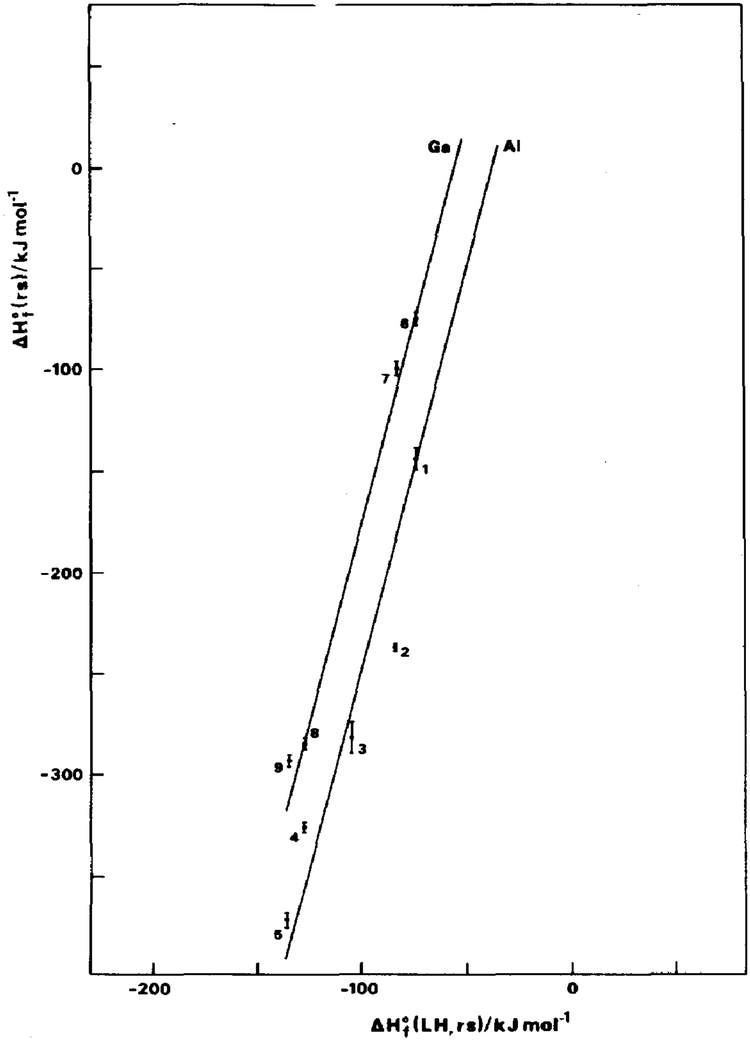

Fig. 9. $\Delta H_f^0[ML_3, rs]$ vs. $\Delta H_f^0(LH, rs)$ for M = Al and Ga. Point numbers correspond to the following ligands: 1 = Me, 2 = Et, 3 = n-Pr, 4 = n-Bu, 5 = i-Bu, 6 = Me, 7 = Et, 8 = n-Bu, 9 = i-Bu.

substances than for zinc alkyls [15]. As there is no reason to suspect the experimental values, the plot in Fig. 8 calls into question the usefulness of the correlation for these substances. It is assumed that all the ligands belong to the same family (eq. 21; r = 0.995).

$$\Delta H_f^0[\mathrm{HgR_2, rs}] = (1.685 \pm 0.063)\Delta H_f^0(\mathrm{RH, rs}) + (151.9 \pm 8.3) \qquad (21)$$

The correlation can be made by use of gas phase data only, since the vaporization or sublimation enthalpies of most compounds are available [2,14,16]. A much poor fit is observed, supporting the views stated above on the intermolecular compensation (see the remarks following Scheme 1

It was no surprise to observe (Fig. 9) some serious scatter in the plot for aluminium alkyls, since most of these data [14] were derived from static bomb combustion experiments. The figure also shows the correlation for the gallium analogues [14], obtained by using the three points for the n-alkyls. The slope (eq. 22) is unexpected, but the fit is fair.

$$\Delta H_f^0[\mathrm{GaR_3, rs}] = (4.131 \pm 0.257)\Delta H_f^0(\mathrm{RH, rs}) + (239.4 \pm 25.1) \qquad (22)$$

The line for AlR_3 was drawn through the point for $AlMe_3$ (derived from a reaction-solution study) and parallel to that for GaR_3. The large deviations observed for $AlEt_3$ and $Al(n\text{-}Bu)_3$ are probably due to experimental errors. Interestingly, an older value for $\Delta H_f^0(\mathrm{AlEt_3, l})$, − 157 ± 21 kJ $\mathrm{mol^{-1}}$ [17], is in much better agreement with the line in Fig. 9.

Final remarks

We summarize below the main conclusions drawn from the discussion and the examples presented above:

1. The existence of a linear correlation between enthalpies of formation of a given series of complexes and enthalpies of formation of ligands LH or LH_m mean that there must be intramolecular compensations, i.e. variations in metal–ligand and ligand–hydrogen bond dissociation enthalpies must follow nearly parallel trends.
2. Compensation of vaporization and sublimation enthalpies is also likely, but is less important than the intramolecular compensation.
3. In complexes of the type MX_nL_m, where L is a neutral ligand (e.g. arene or oxygen donor), the plot can be constructed by using $\Delta H_f^0(\mathrm{L, rs})$ instead of $\Delta H_f^0(\mathrm{LH, rs})$ or $\Delta H_f^0(\mathrm{LH}_m\mathrm{, rs})$, whenever metal–ligand bond dissociation enthalpies are expected to be relatively constant for the whole series of complexes.
4. A "family" is a series of complexes (or ligands) fitted by the same correlation. Each family is defined by the intercept of the straight line, which in turn is determined by the difference between metal–ligand and ligand–hydrogen bond dissociation enthalpies.
5. Although the slope of a correlation reflects the number of ligands L coordinated to the metal atom, its value is also affected by other structural features of the complex (e.g. the existence of dimers with bridged ligands).
6. Destabilizing effects, such as steric strain, can in principle be quantified by comparing the experimental value for the enthalpy of formation of the complex with the "ideal" value calculated from the correlation. This correlation is obtained from data where those effects are expected to be negligible.

7. The steric destabilization of a moiety may not be reflected in the correlation if the corresponding increase in the enthalpy of formation of the molecule is offset by an enthalpy decrease caused by other changes (not necessarily structural) in the molecule.

The use of the linear correlations to predict or to assess thermochemical data for organometallic and coordination compounds could have been illustrated with other examples besides those described in this paper, but a different choice would not change the conclusions. What is important to stress is that definition of the limits of application of the method are still hindered by the lack of suitable data. A particularly important example concerns the prediction of enthalpies of formation of metallacycles, for which more detailed information is required in order to define a family. In other cases, it is uncertain if a less satisfactory correlation indicates a limitation of the method, reflects poor quality experimental data, or results from a wrong assignment of a family. Incidentally, the correlations can often be improved by defining a larger number of families (e.g., for $MoCp_2L_2$ the correlation for oxygen and sulfur ligands could be split into two), but then the method would lose some of its practical interest. Interesting insights into the problems raised by conclusions 5 and 6 can be obtained by determining for example the enthalpies of formation of selected homoleptic metal alkoxides. In conclusion, although the present study has provided some rules for applying the method more correctly, some of these rules must still be tested with reliable thermochemical data.

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