Standard Heats of Formation and M–C Bond Energy Terms for Some Homoleptic Transition Metal Alkyls MR_n†

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Summary The heats of alcoholysis in isopropyl alcohol of the d^0 Ti or Zr compounds MR_4 ($R = Me_3SiCH_2$, Me_3CCH_2, or $PhCH_2$), $M(NR'_2)_4$ ($R' = Me$ or Et), and MCl_4 (and some Hf analogues) have been measured, as well as the heats of solution in Pr^iOH of $M(OPr^i)_4$, RH, R'_2NH, or HCl; from these and subsidiary data standard heats of formation and thermochemical mean bond energy terms have been derived [M–X in kcal mol^{-1}: Ti–$C_{neopentyl}$, 44; Ti–C, 63; Ti–N, 81; Ti–O, 115; Zr–$C_{neopentyl}$, 54; Zr–C, 74; Zr–N, 90; Zr–O, 132; Hf–$C_{neopentyl}$, 58; Hf–N, 95; Hf–O, 137].

Until recently it was thought that transition metal alkyls are inherently thermally unstable and that 'stabilising' ligands such as tertiary phosphines are required in order to obtain characterisable compounds, *e.g.*, *trans*-[PtCl(Me)($PPh_3)_2$]. For compounds of this complexity it is difficult from calorimetric observations to obtain standard heats of formation (ΔH_f°), and *a fortiori* to apportion energy and thus compute a meaningful M–C thermochemical bond energy term, *E*(M–C). Nevertheless, such data are required to rationalise results on, for example, the relative thermal stability of geometrically related main group and transition metal akyls.

The synthesis of various series of homoleptic metal alkyls, *i.e.*, compounds of type MR_n,[1] has considerably simplified the thermochemical problem. We now report calorimetric results on the series of tetrahedral or distorted tetrahedral d^0 complexes MR_4 (M = Ti, Zr, or Hf; $R = Me_3SiCH_2$, Me_3CCH_2, or $PhCH_2$),[1] $M(NMe_2)_4$,[2] $M(NEt_2)_4$,[2] and $M(OPr^i)_4$.[2]

It was found by product analysis, ^1H n.m.r. spectroscopy, and calorimetry (the shape of the cooling curve) that each metal(IV) alkyl, dialkylamide, or chloride undergoes rapid and quantitative alcoholysis by an excess (*ca.* 2000 mol) of Pr^iOH at 25 °C to yield $M(OPr^i)_4$ (solution in Pr^iOH) and the appropriate alkane, amine, or HCl dissolved in Pr^iOH. Pr^iOH was used, rather than a primary alcohol, because of the monomeric and unassociated nature of $M(OPr^i)_4$,[2] and the simplicity of the ^1H n.m.r. spectra. The calorimeter was similar in design to one described earlier, but approximately $^1/_{10}$th the capacity[3]; *ca.* 30 ml Pr^iOH was used for each run. Measurements were made of heats of alcholysis of ML_4 (ΔH_{obs}), and heats of solution in Pr^iOH of the products; the mean of at least five separate results was

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† Reprints not available.

TABLE. Thermochemical data (kcal mol^{-1}) for some d^0 complexes MX_4

Compound (state)	ΔH_{obs}	ΔH_{vap}	$\Delta H_{\mathrm{f}}^{0}$[a]	$\bar{E}$(M–X)[b]
$\mathrm{TiCl_4}$ (l)	−52·5 ± 1·2	9·8[4]	−192·2 ± 1·0[4]	102·7[4]
$\mathrm{Ti(CH_2SiMe_3)_4}$ (l)	−151·8 ± 1·4	18	−205·9 ± 1·5	64[c]
$\mathrm{Ti(CH_2CMe_3)_4}$ (c)	−203 ± 1·8	21	−58·6 ± 1·9	44
$\mathrm{Ti(CH_2Ph)_4}$ (c)	−164·4 ± 1·6	21	+77·6 ± 1·7	63
$\mathrm{Ti(NMe_2)_4}$ (l)	−78·0 ± 0·9	14	−77·3 ± 1·3	81
$\mathrm{Ti(NEt_2)_4}$ (l)	−80·6 ± 0·7	16[9]	−132 ± 1	81[d]
$\mathrm{Ti(OPr^i)_4}$ (l)	−16·2 ± 0·2	17[9]	−390 ± 2	115[d]
$\mathrm{ZrCl_4}$ (c)	−41·7 ± 1·6	26·3[4]	−234·35 ± 0·1[4]	117·4[4]
$\mathrm{Zr(CH_2SiMe_3)_4}$ (l)	−173·3 ± 4·8	18	−215·6 ± 4·8	75
$\mathrm{Zr(CH_2CMe_3)_4}$ (c)	−230·2 ± 3·8	21	−62·6 ± 3·8	54
$\mathrm{Zr(CH_2Ph)_4}$ (c)	−181·4 ± 0·1	21	+63·4 ± 0·6	74
$\mathrm{Zr(NMe_2)_4}$ (c)	−98·7 ± 0·9	17	−87·8 ± 1·3	91
$\mathrm{Zr(NEt_2)_4}$ (l)	−112·3 ± 0·1	16	−131·3 ± 0·7	89
$\mathrm{Zr(OPr^i)_4}$ (c)	−7·5 ± 0·3	20	−430 ± 2·0	132
$\mathrm{HfCl_4}$ (c)	−53·2 ± 1·7	25·3[4]	−236·7 ± 1·0[4]	118·9[4]
$\mathrm{Hf(CH_2CMe_3)_4}$ (c)	−230·1 ± 5·6	21	−75·6 ± 5·6	58
$\mathrm{Hf(NEt_2)_4}$ (l)	−104·1 ± 5·2	16	−151·4 ± 5·2	95
$\mathrm{Hf(OPr^i)_4}$ (c)	−8·0 ± 0·5	20	−442·5 ± 1·8	137

[a] The error on $\Delta H_{\mathrm{f}}^{0}$ (g) is assumed to be ± 8 kcal mol^{-1}. [b] ± 2 kcal mol^{-1}; an alternative way of describing bond strengths is in terms of the mean bond dissociation energy $\bar{D}$(M–X) when, *e.g.*, $\bar{D}(\mathrm{Ti–C_{neopentyl}}) = 50$, $\bar{D}(\mathrm{Ti–C_{benzyl}}) = 54$, $\bar{D}(\mathrm{Ti–NMe_2}) = 77$, $\bar{D}$(Ti–O) = 110 kcal mol^{-1}; the difference between the neopentyl and benzyl systems is disguised in the $\bar{D}$ procedure by the considerably greater stability of $\mathrm{Ph\dot{C}H_2}$ compared with $\mathrm{MeC\dot{C}H_2}$. [c] $\bar{E}$(Ti–Me) has been estimated as *ca.* 60 ± 5 kcal mol^{-1} in $[\mathrm{Ti(C_5H_5\text{-}\eta^5)_2Me_2}]$ (V. I. Telnoi, I. B. Rabinovich, V. D. Tikhanov, V. N. Latyaeva, L. I. Vysginskaya, and G. A. Razuvaev, *Dokl. Akad. Nauk S.S.S.R.*, 1967, **174**, 1374). [d] Using different calorimetric reactions mean bond energies D(Ti-N) and D(Ti–O) have been estimated as 73 and 103 kcal mol^{-1}, respectively.[9]

taken for each, the quoted uncertainty (Table) being twice the standard deviation from the mean. Heats of solution in $\mathrm{Pr^iOH}$ were measured as follows (in kcal mol^{-1}): $\mathrm{Me_2NH}$ (l), −2·7 ± 0·2; $\mathrm{Et_2NH}$ (l), −2·75 ± 0·1; $\mathrm{Me_2NH.HCl}$ (c), +5·39 ± 0·24; $\mathrm{Et_2NH.HCl}$ (c), +5·13 ± 0·23; $\mathrm{Me_4C}$ (l), +0·45 ± 0·01; $\mathrm{Me_4Si}$ (l), +0·67 ± 0·01; and PhMe (l), +0·97 ± 0·03. $\Delta H_{\mathrm{f}}^{0}$ HCl (in $\mathrm{Pr^iOH}$) was calculated as −35·83 ± 0·81 kcal mol^{-1} from the measured ΔH (−19·86 ± 0·71 kcal mol^{-1}) for: HCl (in $\mathrm{Pr^iOH}$) + $\mathrm{Et_2NH}$ (l) = $\mathrm{Et_2NH.HCl}$ (in $\mathrm{Pr^iOH}$). $\Delta H_{\mathrm{f}}^{0}$ $\mathrm{M(OPr^i)_4}$ (l or c) (Table) was obtained from the heat of reaction of $\mathrm{MCl_4}$ (l or c) and excess of $\mathrm{Pr^iOH}$ (l) and the known[4] $\Delta H_{\mathrm{f}}^{0}$ $\mathrm{MCl_4}$; the $\Delta H_{\mathrm{f}}^{0}$ for all other $\mathrm{ML_4}$ species were calculated from $\Delta H_{\mathrm{f}}^{0}$ $\mathrm{M(OPr^i)_4}$.

Subsidiary $\Delta H_{\mathrm{f}}^{0}$ (kcal mol^{-1}) data from the literature are for $\mathrm{TiCl_4}$ (l), −192·2 ± 1·0;[4] $\mathrm{ZrCl_4}$ (c), −234·35 ± 0·1;[4] $\mathrm{HfCl_4}$ (c), −236·7 ± 1·0;[4] HCl (g), −22·06 ± 0·01;[4] HCl ($\mathrm{55H_2O}$), −39·54 ± 0·01;[4] $\mathrm{H_2O}$ (g), −57·80 ± 0·01;[4] $\mathrm{NH_3}$ (g), −11·02 ± 0·1;[4] $\mathrm{Me_2NH}$ (l), −10·5 ± 0·12;[5] $\mathrm{Me_2NH}$ (g), −4·43 ± 0·12;[5] $\mathrm{Et_2NH}$ (l), −24·78 ± 0·29;[5] $\mathrm{Et_2NH}$ (g), −17·16 ± 0·31;[5] $\mathrm{Me_2NH.HCl}$ (c), −69·3 ± 0·10;[6] $\mathrm{Et_2NH.HCl}$ (c), −85·6 ± 0·20;[7] $\mathrm{Pr^iOH}$ (l), −76·02 ± 0·12;[5] $\mathrm{Pr^iOH}$ (g), −65·12 ± 0·13;[5] $\mathrm{CH_4}$ (g), −17·89 ± 0·07;[5] $\mathrm{Me_4C}$ (l), −34·1 ± 1·0;[5] $\mathrm{Me_4C}$ (g), −40·27 ± 0·25;[5] $\mathrm{Me_4Si}$ (l), −64·5 ± 2·3;[8] $\mathrm{Me_4Si}$ (g), −58·2 ± 2·3;[8] PhMe (l), +2·91 ± 0·10;[5] PhMe (g), +11·99 ± 0·10;[5] Ti (g), 112·3;[4] Zr (g), 145·5;[4] and Hf (g), 148·0.[4] Heats of fusion of 3 kcal mol^{-1} are assumed; latent heats of vaporisation were chosen (see Table) on the basis of measurements for $\mathrm{TiCl_4}$,[4] $\mathrm{ZrCl_4}$,[4] $\mathrm{Ti(OPr^i)_4}$,[9] and $\mathrm{Ti(NEt_2)_4}$,[9] and Trouton's method of calculations. As the latter gave results *ca.* 5 kcal mol^{-1} lower than the available[4,9] experimental results, for the other compounds a similar adjustment was made. Because of the various assumptions, we place an upper limit of ±8 kcal mol^{-1} on the error on the quoted $\Delta H_{\mathrm{f}}^{0}$ (g) with consequential maximum error of ±2 kcal mol^{-1} in $\bar{E}$(M–X). Subsidiary $\bar{E}$(X–Y) data (kcal mol^{-1}) used were as follows: O–H (based on $\mathrm{H_2O}$), 110·8; N–H (based on $\mathrm{NH_3}$), 93·4; C–H (based on $\mathrm{CH_4}$), 99·3; H–Cl (based on HCl), 103·2; Ti–Cl (based on $\mathrm{TiCl_4}$), 102·7; Zr–Cl (based on $\mathrm{ZrCl_4}$), 117·4; and Hf–Cl (based on $\mathrm{HfCl_4}$), 118·9. Data on related complexes, such as $\mathrm{V^{IV}}$ or $\mathrm{Cr^{IV}}$ analogues, can now be obtained by similar measurements. The procedure for calculating thermochemical mean bond energy terms $\bar{E}$(M–X) has been described before for complexes of Si, Ge, and Sn.[3]

The results are shown in the Table. For Ti, Zr, and Hf mean bond strengths decrease in the sequence M–O > M–Cl > M–N > M–C, and the values are monotonically higher for Zr than Ti compounds by *ca.* 15%, and slightly higher for Hf than Zr. A quite surprising result is that with neopentyl, the smallest of the bulky alkyl ligands, a very considerably weakened M–C bond is found, which must be attributable to a substantial steric effect. We note that $\bar{E}$(M–C) for these transition metal alkyls are not unduly low and their relation to corresponding $\bar{E}$(M–N), $\bar{E}$(M–Cl), or $\bar{E}$(M–O) bonds is not significantly different from that found for the *p*-block element analogues Si, Ge, or Sn;[3] however, for these the heavier element forms the weaker bonds.

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[1] *Cf.* P. J. Davidson, M. F. Lappert, and R. Pearce, *Accounts Chem. Res.*, 1974, **7**, 209.

[2] *Cf.* D. C. Bradley, *Adv. Inorg. Chem. Radiochem.*, 1972, **15**, 259.

[3] J. C. Baldwin, M. F. Lappert, J. B. Pedley, and J. A. Treverton, *J. Chem. Soc.* (*A*), 1967, 1980; J. C. Baldwin, M. F. Lappert, J. B. Pedley, and J. S. Poland, *ibid.*, 1972, 1943.

[4] 'Selected Values of Chemical Thermodynamic Properties', Nat. Bur. Stand. Tech. Note 270, U.S. Government Printing Office, Washington, D.C.

[5] J. D. Cox and G. Pilcher, 'Thermochemistry of Organic and Organometallic Compounds', Academic Press, London, 1970.

[6] Using $\Delta H_{\mathrm{f}}^{0}$ ($\mathrm{Me_2NH.HCl}$, aq) from ref. 4, and measurement of ΔH_{soln} in 1 M HCl ($\mathrm{Me_2NH.HCl}$, c).

[7] P. A. Fowell and C. T. Mortimer, *J. Chem. Soc.*, 1959, 2913.

[8] J. B. Pedley and B. S. Iseard, 'Computer Analysis of Thermochemical Data', CATCH Tables, Silicon Compounds, School of Molecular Sciences, University of Sussex, Brighton, Sussex, 1972.

[9] D. C. Bradley and M. J. Hillyer, *Trans. Faraday Soc.*, 1966, **62**, 2374.