# Heat of Formation of Pentamethyltantalum and Hexamethyltungsten

By Festus A. Adedeji, Joseph A. Connor,* and Henry A. Skinner
(*Department of Chemistry, University of Manchester, Manchester* M13 9PL)

and Lee Galyer and Geoffrey Wilkinson
(*Department of Chemistry, Imperial College, London* SW7 2AY)

*Summary* Mean bond dissociation energy values, $\bar{D}$(Ta–Me) = 261 ± 6 kJ mol$^{-1}$ (62 ± 2 kcal mol$^{-1}$) and $\bar{D}$(W–Me) = 159 ± 7 kJ mol$^{-1}$ (38 ± 2 kcal mol$^{-1}$) have been derived from the heats of formation, $\Delta H_f^\circ$($TaMe_5$, liq.) = 169·8 ± 26 kJ mol$^{-1}$ and $\Delta H_f^\circ$($WMe_6$, liq.) = 738·7 ± 34 kJ mol$^{-1}$, obtained from measurement of the heats of hydrolysis of solutions of $TaMe_5$ and $WMe_6$.

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The strength of metal–carbon σ-bonds is of importance in regard to the role of such linkages in many reactions between organic molecules and metals. The synthesis of the permethyl metal compounds, $MMe_n$ (M = Ta,[1] $n = 5$; M = W, Re,[2] $n = 6$), that are liable to spontaneous decomposition in the solid state,[3] provides an opportunity to determine the mean bond dissociation energy of the simplest of transition metal alkyls in the absence of special factors that might stabilise M–C σ-bonds as, for example, in $M(CH_2R)_n$ (R = Ph, $CMe_3$, or $SiMe_3$).

Solutions of $TaMe_5$ and $WMe_6$ in isopentane (*ca.* 40 mg cm$^{-3}$) were hydrolysed at *ca.* 273 K in moist diethyl ether ($TaMe_5$) or in aqueous ammonia under iso-octane ($WMe_6$).

The metal was recovered from the aqueous layer as the oxide [$Ta_2O_5$ or, *via* $(NH_4)_2WO_4$, $WO_3$]. Ammonia was used for $WMe_6$ as the hydrolysis in moist ether is very slow, possibly because of the formation of ether soluble intermediates such as $WOMe_4$.

The measured enthalpy of hydrolysis, $\Delta H_{273}(TaMe_5) = -(849 \pm 26)$ kJ mol$^{-1}$, is attributed to reaction (1). The

$$TaMe_5 \text{ (isopentane solution)} + 2{\cdot}5H_2O\text{(liq.)} + \text{excess aq. } Et_2O \rightarrow 0{\cdot}5Ta_2O_5\text{(ppt.)} + 5CH_4\text{(isopentane, } Et_2O) \quad (1)$$

corresponding quantity, $\Delta H_{273}(WMe_6) = -(1228 \pm 34)$ kJ mol$^{-1}$, relates to the hydrolysis reaction (2). To adjust the

$$WMe_6 \text{ (isopentane solution)} + 2H_2O\text{(liq.)} + 2OH^- \text{(aq.)} \rightarrow WO_4^{2-} \text{(aq.)} + 6CH_4 \text{ (isopentane, iso-octane)} \quad (2)$$

measured $\Delta H_{273}$ to apply to hydrolysis in the absence of organic solvents at 298 K, we have assumed negligible heats of mixing of liquid $TaMe_5$ and $WMe_6$ with isopentane and that $\Delta H_{298} = (\Delta H_{273} - 4)$ kJ mol$^{-1}$ ($\Delta C_p$ *ca.* $-160$ J K$^{-1}$ mol$^{-1}$). No thermal corrections were made for solution of methane in ether or iso-octane solvents because they were found to be negligible in the open system used, as expected.† Using recommended[4] standard $\Delta H°$ values,‡ the adjusted $\Delta H_{298}$ correspond to $\Delta H°(TaMe_5, \text{liq.}) = (169{\cdot}8 \pm 26)$ kJ mol$^{-1}$ and $\Delta H°(WMe_6, \text{liq.}) = (738{\cdot}7 \pm 34)$ kJ mol$^{-1}$. Values of $\Delta H_{vap}$ are not available and estimates [$\Delta H_{vap}(WMe_6, \text{liq.})$ *ca.* 33 kJ mol$^{-1}$ and $\Delta H_{vap}$ ($TaMe_5$, liq.) *ca.* 42 kJ mol$^{-1}$] were used together with recommended[4] $\Delta H_f°$ values§ to calculate the enthalpies of disruption leading to mean bond dissociation energy values $\bar{D}$(Ta–Me) = (261 ± 6) kJ mol$^{-1}$ (62·4 ± 2 kcal mol$^{-1}$), and $\bar{D}$(W–Me) = (159 ± 7) kJ mol$^{-1}$ (38·1 ± 2 kcal mol$^{-1}$).

The value of $\bar{D}$(W–Me) in $WMe_6$ is slightly less than that for $\bar{D}$(W–CO) in $W(CO)_6$[5] (178·2 ± 3·3 kJ mol$^{-1}$), and there is some evidence[6] for steric strain in $WMe_6$ arising from interference between methyl groups. Mean bond enthalpy values cannot, of course, be directly correlated with the experimentally observed thermal stability of peralkyls. It seems probable that the energy required to initiate decomposition is $< \bar{D}$(M–Me) and hydride transfer may be important, even for the methyl group {*cf.* the formation[7] of $[Ta(CH_2CMe_3)_3(CHCMe_3)]$}. The present results, together with those[8] for $M(CH_2R)_4$ (M = Ti, Zr, or Hf; R = Ph, $CMe_3$, or $SiMe_3$) imply that the M–H bonds formed by $\beta$-elimination from $\sigma$-alkyl compounds are thermodynamically strong [*e.g.*, $\bar{D}$(Ta–H) > 370 kJ mol$^{-1}$]. The progression of mean bond enthalpy values $\bar{D}$(M–Z) ($Z = F > OR > Cl > NR_2 > CR_3$) observed[8] for M = Ti, Zr, or Hf appears to apply to other groups,[4,9] so that the average bond energy of $MoMe_6$ should be less than that of $WMe_6$ while that of $UMe_6$ should be higher; $NbMe_5$ is reported[1] to be less stable than $TaMe_5$.

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† In a closed system, $\Delta H°_{solution}$ ($CH_4$–$Et_2O$) = $-5{\cdot}9 \pm 0{\cdot}4$ kJ mol$^{-1}$ (A. S. Carson, W. Carter, and J. B. Pedley, *Proc. Roy. Soc.*, 1961, **260A**, 550).

‡ $\Delta H°_f$/kJ mol$^{-1}$ for: $H_2O$ (liq.) $-285{\cdot}83$, $OH^-$ (aq.) $-230{\cdot}02$, $CH_4$ (g.) $-74{\cdot}85$, $WO_4^{2-}$ (aq.) $-1075{\cdot}90$, and $Ta_2O_5$ (c) $-(2047 \pm 1{\cdot}5$

§ $\Delta H°_f$/kJ mol$^{-1}$ for: W (g.) 851·03 ± 6, Ta (g.) 786·6 ± 4, and Me (g.) 146·0 ± 0·6.

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