

Heat of Formation of Bis(η -cyclopentadienyl)dimethyltungsten and Bis(η -cyclopentadienyl)dimethylmolybdenum

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Summary Bond-enthalpy contribution values $D(\text{Mo-Me}) = 149.5 \text{ kJ mol}^{-1}$ and $D(\text{W-Me}) = 197.8 \text{ kJ mol}^{-1}$ have been derived from the standard enthalpies of formation $\Delta H_f^\circ [\text{Mo}(\eta\text{-C}_5\text{H}_5)_2\text{Me}_2, \text{c}] = (283.8 \pm 3.8) \text{ kJ mol}^{-1}$ and $\Delta H_f^\circ [\text{W}(\eta\text{-C}_5\text{H}_5)_2\text{Me}_2, \text{c}] = (295.6 \pm 3.5) \text{ kJ mol}^{-1}$ obtained from measurements of the reaction enthalpies of $\text{Mo}(\eta\text{-C}_5\text{H}_5)_2\text{Me}_2(\text{c})$ and $\text{W}(\eta\text{-C}_5\text{H}_5)_2\text{Me}_2(\text{c})$ in an aqueous solution of hydrochloric acid.

under 1 atm pressure,³ it can be assumed that all methane formed leaves the reaction vessel. The measured value for the solution enthalpy of $\text{M}(\eta\text{-C}_5\text{H}_5)_2\text{Cl}_2$ (c) in 8.3 M hydrochloric acid is $(12.9 \pm 1.1) \text{ kJ mol}^{-1}$ for the molybdenum compound and 0 kJ mol^{-1} for the tungsten compound.

Using the relevant literature⁴ data† and the values of $\Delta H_f^\circ [\text{Mo}(\eta\text{-C}_5\text{H}_5)_2\text{Cl}_2, \text{c}]$ and $\Delta H_f^\circ [\text{W}(\eta\text{-C}_5\text{H}_5)_2\text{Cl}_2, \text{c}]$ derived by Tel'noi *et al.*⁵ we can calculate the standard enthalpies of formation of $\text{Mo}(\eta\text{-C}_5\text{H}_5)_2\text{Me}_2$ (c) and $\text{W}(\eta\text{-C}_5\text{H}_5)_2\text{Me}_2$ (c) (Table).

The values of the sublimation enthalpies of $\text{M}(\eta\text{-C}_5\text{H}_5)_2\text{Me}_2$ and $\text{M}(\eta\text{-C}_5\text{H}_5)_2\text{Cl}_2$ are not available for either the molybdenum or the tungsten compound. However, they can be estimated from published results for the zirconium analogues,⁶ assuming that the difference between the sublimation enthalpies of the dichlorides and the dimethyls is approximately the same for the tungsten and molybdenum compounds.

$$\Delta H_f^\circ [\text{M}(\eta\text{-C}_5\text{H}_5)_2\text{Cl}_2, \text{c}] - \Delta H_f^\circ [\text{M}(\eta\text{-C}_5\text{H}_5)_2\text{Me}_2, \text{c}] = 20.9 \pm 8.4 \text{ kJ mol}^{-1}$$

Using this value we can derive bond-enthalpy contribution differences between M-Cl and M-Me (Table). Moreover, if we take Tel'noi's values⁵ for M-Cl we can obtain values for $D(\text{Mo-Me})$ and $D(\text{W-Me})$ (Table).

The result for $D(\text{W-Me})$ is higher than the known mean bond dissociation energy $D(\text{W-Me})$ in WMe_6 ,⁷ 159 kJ mol^{-1} . This is probably a consequence of the steric strain in WMe_6 , which is not so noticeable in $\text{W}(\eta\text{-C}_5\text{H}_5)_2\text{Me}_2$.^{7,8} To our knowledge no other values for $D(\text{Mo-Me})$ are available in the literature. Our value is consistent with that obtained for $D(\text{W-Me})$ since the difference between $D(\text{Mo-Me})$ and $D(\text{W-Me})$, ca. 48.3 kJ mol^{-1} , is of the same order of magnitude of bond-enthalpy contribution differences between $D(\text{M-L})$ values in other similar compounds of tungsten and molybdenum.⁹

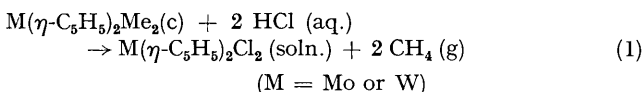
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THE importance of the knowledge of metal-carbon σ -bond strengths in relation to the involvement of such bonds in many reactions of wide application is well recognized.¹ Despite this recognition only a limited number of those bond strengths is available. For this reason we have measured the metal-carbon bond-enthalpy contributions by reaction-solution calorimetry, in compounds of the type $\text{M}(\eta\text{-C}_5\text{H}_5)_2\text{R}_2$, where M = Mo or W and R = alkyl.

TABLE. Enthalpy values in kJ mol^{-1} for $\text{M}(\eta\text{-C}_5\text{H}_5)_2\text{Me}_2$.

M	$-\Delta H_1$	$\Delta H_f^\circ(\text{c})$	$D(\text{M-Cl}) - D(\text{M-Me})$	$D(\text{M-Me})$
Mo	202.1 ± 2.8	283.8 ± 3.8	154.7 ± 4.5	149.5
W	191.3 ± 2.3	295.6 ± 3.5	148.2 ± 4.5	197.8

The enthalpies of reaction (1) (adapted from the one reported by Green *et al.*²) at 298.15 K were measured using an LKB 8700 Reaction and Solution Precision Calorimeter (Table). In the reactions for both M = Mo and M = W the methyl groups are replaced by chlorine atoms but the cyclopentadienyl rings remain unaffected.



A large excess of hydrochloric acid solution was used (8.3 M) and its concentration did not change significantly during the course of the experiments. However, since the solubility of methane in water $x_2 = \text{ca. } 2.5 \times 10^{-5}$

† $\Delta H_f^\circ/\text{kJ mol}^{-1}$ for: HCl (aq., 8.3 M) $- 156.82$, $\text{CH}_4(\text{g}) - 74.52 \pm 0.42$, Cl (g) 121.00 ± 0.13 , and $\text{CH}_3(\text{g}) 145.69 \pm 0.84$.

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