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BOND-ENTHALPY CONTRIBUTIONS IN $M(\eta\text{-}C_5H_5)_2L_2$ COMPLEXES (M = Mo, W; L = H, CH_3, Cl)

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Summary

Reaction—solution calorimetric measurements of reactions of $M(\eta\text{-}C_5H_5)_2H_2$ (c) (M = Mo, W) with carbon tetrachloride led to bond-enthalpy contributions $\bar{D}$(Mo—H) 251.4 kJ mol^{-1} and $\bar{D}$(W—H) 305.2 kJ mol^{-1}.

Introduction

A knowledge of bond strengths, particularly those of metal-to-carbon bonds, is paramount in elucidation the mechanisms of reactions involving organometallic compounds. Previously we reported [1] the bond-enthalpy contributions $\bar{D}(M—CH_3)$ in $M(\eta\text{-}C_5H_5)_2(CH_3)_2$ (M = Mo, W), obtained from thermochemical measurements using reaction-solution calorimetry. The present paper deals with an extension of that work to the compounds $M(\eta\text{-}C_5H_5)_2H_2$ (M = Mo, W) in order to determine the bond-enthalpy contributions $\bar{D}$(M—H).

Tel'noi et al. [2] had already obtained the standard enthalpies of formation ΔH_f^0 [$M(\eta\text{-}C_5H_5)_2L_2$ (c)] (M = Mo, W; L = H, Cl) from which such bond-enthalpy contributions can be derived, but they used combustion calorimetry which is not the best technique for this type of compounds, since they are usually unstable to oxidation and the final state of their combustion is not easily determined. We thus considered it worthwhile to determine the values by use of a reaction-solution calorimeter.

Experimental

Calorimeters

The heats of reactions 1 and 2 were measured in the reaction-solution calorimeter previously described [3]. To ensure an inert atmosphere in the calorimetric vessel, pure nitrogen was bubbled through the solvent (carbon tetrachloride; 125 cm^3) for 45 min before each run. The solution enthalpy of stoichiometric amounts of chloroform in carbon tetrachloride was determined in an LKB 8700 reaction and solution precision calorimeter.

Compounds

The $M(\eta\text{-}C_5H_5)_2H_2$ (M = Mo, W) samples were prepared as described by Green et al. [4]. The compounds were resublimed before use and their purity checked by spectroscopic analysis. B.D.H. Analar carbon tetrachloride and chloroform were dried by refluxing over anhydrous calcium chloride and distilled before each experiment.

Reactions

The final state of reaction 2 was demonstrated by Green et al. [4]. Using a Perkin—Elmer F 11 gas chromatograph with a 15% silicone grease/85% chromosorb P (80—100) column, we were able to identify the volatile product of reaction 1 as $CHCl_3$. No dichloromethane was detected.

Results and discussion

The measured enthalpies of reactions

$$Mo(\eta\text{-}C_5H_5)_2H_2\ (c) + 2\ CCl_4\ (l) \rightarrow Mo(\eta\text{-}C_5H_5)_2Cl_2\ (c) + 2\ CHCl_3\ (soln) \tag{1}$$

and

$$W(\eta\text{-}C_5H_5)_2H_2\ (c) + 2\ CCl_4\ (l) \rightarrow W(\eta\text{-}C_5H_5)_2Cl_2\ (c) + 2\ CHCl_3\ (soln) \tag{2}$$

are shown in Tables 1 and 2 respectively. The value obtained for the heat of solution of $CHCl_3$ in CCl_4 is 0.89 ± 0.05 kJ mol^{-1} (mean of four runs).

The values of $\Delta H_f^\circ[M(\eta\text{-}C_5H_5)_2H_2(c)]$ and $\bar{D}(M—Cl) - \bar{D}(M—H)$ both for Mo and for W (Table 3) were obtained from the mean values of Tables 1 and 2 and

TABLE 1

REACTION OF $Mo(\eta\text{-}C_5H_5)_2H_2(c)$ WITH $CCl_4(l)$

ϵ = calibration constant; ΔT = measured temperature difference.

Mass (g)	ϵ (JK^{-1})	ΔT (K)	$-\Delta H_r$ (kJ mol^{-1})
0.117905	221.03	0.7400	316.51
0.157890	227.18	0.9960	326.96
0.192800	228.28	1.1620	313.88
0.178855	229.54	1.0966	321.09
0.206040	228.16	1.2633	319.16

Mean $\Delta H_r = -319.5 \pm 4.4$ kJ mol^{-1}

TABLE 2

REACTION OF $W(\eta\text{-}C_5H_5)_2H_2(c)$ WITH $CCl_4(l)$

c = calibration constant; ΔT = measured temperature difference.

Mass (g)	c (JK^{-1})	ΔT (K)	$-\Delta H_r$ (kJ mol^{-1})
0.158455	226.16	0.6520	294.13
0.161175	222.92	0.6924	302.65
0.166600	230.65	0.6854	299.90
0.122120	218.85	0.5349	302.97
0.110665	222.69	0.4669	296.91

Mean ΔH_r = 299.3 ± 3.4 kJ mol^{-1}

from the following auxiliary data (kJ mol^{-1}): $\Delta H_f^0[CCl_4\ (g)] - \Delta H_f^0[CHCl_3\ (g)]$ = 9.50 ± 1.26 [5]; $\Delta H_v^0(CCl_4)$ = 32.43 ± 0.08 [6]; $\Delta H_v^0(CHCl_3)$ = 30.54 ± 0.42 [6]; $\Delta H_f^0[Mo(\eta\text{-}C_5H_5)_2Cl_2\ (c)]$ = −95.81 ± 2.51 [2]; $\Delta H_f^0[W(\eta\text{-}C_5H_5)_2Cl_2\ (c)]$ = −71.13 ± 2.51 [2]; $\Delta H_s^0[Mo(\eta\text{-}C_5H_5)_2Cl_2] - \Delta H_s^0[Mo(\eta\text{-}C_5H_5)_2H_2]$ = 7.9 ± 6.3 [2]; $\Delta H_s^0[W(\eta\text{-}C_5H_5)_2Cl_2] - \Delta H_s^0[W(\eta\text{-}C_5H_5)_2H_2]$ = 8.4 ± 6.3 [2]; $\Delta H_f^0[H\ (g)]$ = 217.986 ± 0.004 [7]; $\Delta H_f^0[Cl\ (g)]$ = 121.290 ± 0.004 [7]. The earlier [1] $\bar{D}(M—Cl) - \bar{D}(M—CH_3)$ values, together with $\bar{D}(M—Cl) - \bar{D}(M—H)$ led to the differences $D(M—H) - \bar{D}(M—CH_3)$ also presented in Table 3. It is worth mentioning that all these bond-enthalpy contributions were derived independently of $\Delta H_f^0[M(\eta\text{-}C_5H_5)_2Cl_2\ (c)]$ values reported in the literature [2].

If we assume, with Tel'noi et al., that $D(Mo—Cl)$ and $D(W—Cl)$ in the complexes are equal to the mean bond dissociation enthalpies in $MoCl_6$ (303.8 kJ mol^{-1}) and WCl_6 (347.3 kJ mol^{-1}) respectively, an assumption supported by internuclear distance data, then the values of $\Delta\bar{D}$ in column three of Table 3 yield $\bar{D}(Mo—H)$ = 251.4 and $\bar{D}(W—H)$ = 305.2 kJ mol^{-1}. Since these figures depend on the correctness of that assumption, we prefer not to attempt to assign any uncertainty ranges to those bond-enthalpy contributions.

There is no significant difference between these values and those obtained by Tel'noi et al., viz. $\bar{D}(Mo—H)$ 259.0 and $\bar{D}(W—H)$ 287.0 kJ mol^{-1}, although for the tungsten compound the difference may be outside the experimental uncertainty, perhaps reflecting the difficulties of using combustion calorimetry for these compounds. Reaction-solution calorimetry provides a simple and direct alternative route for solving this problem.

TABLE 3

BOND-ENTHALPY CONTRIBUTIONS $\bar{D}(M—L)$

M	ΔH_f^0 $[M(\eta\text{-}C_5H_5)_2H_2,\ (c)]$ (kJ mol^{-1})	$\bar{D}$ (M—Cl) $-\bar{D}$ (M—H) (kJ mol^{-1})	$\bar{D}$ (M—H) $-\bar{D}$ $(M—CH_3)$ (kJ mol^{-1})
Mo	210.3 ± 5.8	52.4 ± 4.1	102.6 ± 6.1
W	214.8 ± 5.0	42.1 ± 3.8	106.4 ± 5.8

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