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# METAL-HYDROGEN AND METAL-IODINE BOND-ENTHALPY CONTRIBUTIONS IN $[M(\eta\text{-C}_5\text{H}_5)_2\text{L}_2]$ ( $M = \text{Mo}, \text{W}; \text{L} = \text{H}, \text{I}$ )<sup>\*</sup>

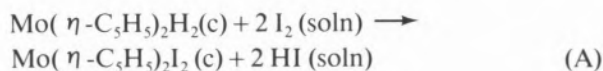
*Reaction-solution calorimetric measurements of reactions of  $[M(\eta\text{-C}_5\text{H}_5)_2\text{H}_2(\text{c})]$  ( $M = \text{Mo}, \text{W}$ ) with  $\text{I}_2$  in toluene, led to bond-enthalpy contributions  $\bar{D}(\text{Mo-I}) = 206.5 \text{ kJ mol}^{-1}$  and  $\bar{D}(\text{W-I}) = 268.3 \text{ kJ mol}^{-1}$ .*

<sup>\*</sup> Presented in part at I Conferência Internacional de Disolucion de No-Electrolitos, Santiago de Compostela, October 1971.

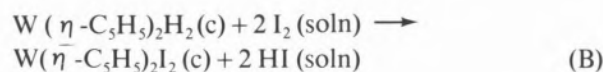
## 1 — INTRODUCTION

The knowledge of metal-ligand bond-enthalpy contributions,  $\bar{D}(\text{M-L})$ , in compounds of the type  $[M(\eta\text{-C}_5\text{H}_5)_2\text{L}'\text{L}'']$  (where M is a transition metal atom and L', L'' can be hydrogen, halogen, aryl, alkyl, etc.) plays a very important role in the prediction and understanding of the chemical reactivities of those compounds. Data such as electronegativities and stretching frequencies are sometimes of little use when trying to explain patterns of reactivity. Our project has thus been initiated with the main purpose of determining the above mentioned bond-enthalpy data, using a reaction-solution calorimetry technique.

In previous articles [1, 2] we reported  $\bar{D}(\text{M-CH}_3)$  and  $\bar{D}(\text{M-H})$  values in the systems  $[M(\eta\text{-C}_5\text{H}_5)_2(\text{CH}_3)_2]$  and  $[M(\eta\text{-C}_5\text{H}_5)_2\text{H}_2]$  ( $M = \text{Mo}, \text{W}$ ) respectively. We now wish to describe the results obtained for the reactions



and



from which  $\bar{D}(\text{Mo-I})$  and  $\bar{D}(\text{W-I})$  values were derived.

## 2 — EXPERIMENTAL

The enthalpies of reactions (A) and (B) were measured in a reaction-solution calorimeter very similar to the one already described in the literature [3]. This consists of a transparent glass Dewar vessel of approximately 150 cm<sup>3</sup> capacity submerged in a thermostatic water bath whose temperature is maintained at  $25.000 \pm 0.001^\circ\text{C}$  by a Tronac PTC 40 Precision Temperature Controller. The temperature changes inside the reaction vessel are recorded to  $10^{-4}$  K at fixed intervals of 10 s by a Hewlett-Packard quartz thermometer (HP 2804 A) and printer (HP 5150 A). The quartz thermometer probe fits tightly in a glass tube filled with silicone oil to improve the thermal conductivity. Constant stirring is obtained by using a SPN precision

agitator connected to a small two-blade glass stirrer inside the calorimeter. The calibrations are made electrically for each experiment with a low temperature coefficient resistance of *ca.* 47  $\Omega$ , placed inside a glass tube filled with silicone oil. The power comes from a Delta Elektronika E 030-3 power supply. The voltage across the heater is measured with a Dana 5000 Digital Voltmeter and the current is determined from the voltage decrease across a 1  $\Omega$  Guildline standard resistance. To select and control the times required for the calibrations a timer-counter with an accuracy of  $\pm 0.01$  s was used.

The  $[\text{M}(\eta\text{-C}_5\text{H}_5)_2\text{H}_2]$  ( $\text{M}=\text{Mo}, \text{W}$ ) samples were sealed under pure nitrogen in thin spheric glass ampoules which were broken in the solution by compression between two glass rings. Before each run and to ensure an inert atmosphere in the calorimeter, pure nitrogen was bubbled through the solution for 45 min.

The heat of the solution of iodine in the solvent (toluene) was determined in an LKB 8700 Reaction and Solution Precision Calorimeter.

The compounds  $[\text{M}(\eta\text{-C}_5\text{H}_5)_2\text{H}_2]$  ( $\text{M}=\text{Mo}, \text{W}$ ) were prepared as described by Green et al. [4] and resublimed. Their purity was checked by IR spectroscopy. B.D.H. 'AnalaR' toluene was dried by refluxing over sodium and distilled before each experiment. B.D.H. 'AnalaR' iodine was used with no further treatment.

Reactions (A) and (B) were adapted from the standard preparation procedure for  $[\text{M}(\eta\text{-C}_5\text{H}_5)_2\text{I}_2]$  ( $\text{M}=\text{Mo}, \text{W}$ ) [5] and their final state was demonstrated by volumetric analysis of the HI formed.

#### 4 — RESULTS AND DISCUSSION\*

The measured enthalpies of reactions (A) and (B) are shown in Tables 1 and 2 respectively. The value obtained for the heat of solution of  $\text{I}_2$  in toluene was  $15.92 \pm 0.16$  (mean of six runs). The heat of solution of HI in toluene was calculated from its solubility data [6] as  $-29.6 \pm 2.3$ . These values, together with  $\Delta H_f^\circ [\text{Mo}(\eta\text{-C}_5\text{H}_5)_2\text{H}_2, \text{c}] = 210.3 \pm 5.8$  [2],  $\Delta H_f^\circ [\text{W}(\eta\text{-C}_5\text{H}_5)_2\text{H}_2, \text{c}] = 214.8 \pm 5.0$  [2] and  $\Delta H_f^\circ (\text{HI}, \text{g}) = 26.359 \pm 0.004$  [7] led to  $\Delta H_f^\circ [\text{Mo}(\eta\text{-C}_5\text{H}_5)_2\text{I}_2, \text{c}] = 69.8 \pm 7.7$  and  $\Delta H_f^\circ [\text{W}(\eta\text{-C}_5\text{H}_5)_2\text{I}_2, \text{c}] = 57.8 \pm 7.4$ . Finally, the mean bond-enthalpy

$\Delta H_f^\circ [\text{W}(\eta\text{-C}_5\text{H}_5)_2\text{I}_2, \text{c}] = 57.8 \pm 7.4$ . Finally, the mean bond-enthalpy

Table 1  
Reaction of  $[\text{Mo}(\eta\text{-C}_5\text{H}_5)_2\text{H}_2(\text{c})]$  with  $\text{I}_2$  in toluene

$[\text{Mo}(\eta\text{-C}_5\text{H}_5)_2\text{H}_2]$ mass/g	$\text{I}_2$ mass/g	$\epsilon / \text{JK}^{-1}$	$\Delta T / \text{K}$	$-H / \text{kJ mol}^{-1}$
0.31433	0.77505	250.56	1.0059	182.95
0.24560	0.61922	245.00	0.7773	176.91
0.25206	0.62547	245.65	0.8040	178.77
0.19340	0.48864	245.54	0.6148	178.08
0.22580	0.55407	241.18	0.7271	177.18
mean $\Delta H = -178.8 \pm 2.2$				

$\epsilon$  = calibration constant;  $\Delta T$  = measured temperature difference.

Table 2  
Reaction of  $[\text{W}(\eta\text{-C}_5\text{H}_5)_2\text{H}_2(\text{c})]$  with  $\text{I}_2$  in toluene

$[\text{W}(\eta\text{-C}_5\text{H}_5)_2\text{H}_2]$ mass/g	$\text{I}_2$ mass/g	$\epsilon / \text{JK}^{-1}$	$\Delta T / \text{K}$	$-H / \text{kJ mol}^{-1}$
0.22724	0.44576	247.69	0.5779	199.10
0.22019	0.38170	247.68	0.5468	194.41
0.21366	0.37432	248.71	0.5294	194.79
0.21762	0.38250	250.64	0.5433	197.76
0.24545	0.42811	250.29	0.5907	190.36
mean $\Delta H = -195.3 \pm 3.0$				

$\epsilon$  = calibration constant;  $\Delta T$  = measured temperature difference.

contribution differences  $\bar{D}(\text{Mo-H}) - \bar{D}(\text{Mo-I}) = 44.9 \pm 3.5$  and  $\bar{D}(\text{W-H}) - \bar{D}(\text{W-I}) = 36.9 \pm 3.6$  were derived, taking into account the experimental values mentioned, as well as  $\Delta H_f^\circ (\text{H}, \text{g}) = 217.986 \pm 0.004$ , [7],  $\Delta H_f^\circ (\text{I}, \text{g}) = 106.763 \pm 0.013$  [7],  $\Delta H_s^\circ [\text{Mo}(\eta\text{-C}_5\text{H}_5)_2\text{I}_2] - \Delta H_s^\circ [\text{Mo}(\eta\text{-C}_5\text{H}_5)_2\text{H}_2] = 7.9 \pm 4.7$  [8],  $\Delta H_s^\circ [\text{W}(\eta\text{-C}_5\text{H}_5)_2\text{I}_2] - \Delta H_s^\circ [\text{W}(\eta\text{-C}_5\text{H}_5)_2\text{H}_2] = 8.4 \pm 4.7$  [8], and the given value for  $\Delta H_f^\circ (\text{HI}, \text{g})$ .

Taking  $\bar{D}(\text{Mo-H})$  and  $\bar{D}(\text{W-H})$  previously obtained [2] we arrive at  $\bar{D}(\text{Mo-I}) = 206.5$  and  $\bar{D}(\text{W-I}) = 268.3$ . Both disagree noticeably with early values reported in the literature [8] (226.4 and 238.5 respectively). These latter values were calculated from combustion calorimetry experiments which does not seem to be 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.

\* All values in  $\text{kJ mol}^{-1}$ .

The  $\bar{D}(\text{Mo-I})$  and  $\bar{D}(\text{W-I})$  derived by us are credible on at least one basis:  $\bar{D}(\text{W-I}) - \bar{D}(\text{Mo-I}) = 61.8$  is of the same order of magnitude of  $\bar{D}(\text{W-L}) - \bar{D}(\text{Mo-L})$  obtained or assumed for  $\text{L} = \text{H}$  [2],  $\text{CH}_3$  [1],  $\text{Cl}$  [8] and  $\text{Br}$  [9], while Tel'noi's difference is about 12 [8].

The set of values so far derived is not enough to establish an overall view of M-L bond-enthalpy contributions in  $[\text{M}(\eta\text{-C}_5\text{H}_5)_2 \text{L}'\text{L}']$  compounds. However, it has already provided routes for possible explanation of their reactivity [10].

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#### RESUMO

Medidas calorimétricas das reações de  $[\text{M}(\eta\text{-C}_5\text{H}_5)_2 \text{H}_2 (c)]$  ( $\text{M} = \text{Mo}, \text{W}$ ) com  $\text{I}_2$ , em tolueno, conduziram aos valores de energias de ligação  $\bar{D}(\text{Mo-I}) = 206.5 \text{ kJ mol}^{-1}$  e  $\bar{D}(\text{W-I}) = 268.3 \text{ kJ mol}^{-1}$ .