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METAL—BROMINE BOND-ENTHALPY CONTRIBUTIONS IN $M(\eta\text{-}C_5H_5)_2Br_2$ COMPLEXES (M = Mo, W)

J.C.G. CALADO, A.R. DIAS and J.A. MARTINHO SIMÕES

Centro de Química Estrutural, Complexo I, Instituto Superior Técnico, Lisboa (Portugal)

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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 tetrabromide in toluene led to bond-enthalpy contributions $\bar{D}$(Mo—Br) = 242.0 kJ mol^{-1} and $\bar{D}$(W—Br) = 298.9 kJ mol^{-1}.

Introduction

In previous papers we reported bond-enthalpy contributions $\bar{D}(M—CH_3)$ [1], $\bar{D}$(M—H) [2], and $\bar{D}$(M—I) [3], respectively, in $M(\eta\text{-}C_5H_5)_2(CH_3)_2$, $M(\eta\text{-}C_5H_5)_2H_2$, and $M(\eta\text{-}C_5H_5)_2I_2$ complexes (M = Mo, W). An obvious extension of this work involved the determination of M—Br bond-enthalpy contributions in $M(\eta\text{-}C_5H_5)_2Br_2$ (M = Mo, W).

A knowledge of metal—halogen bond energies will allow us to derive other $\bar{D}$(Mo—L) and $\bar{D}$(W—L) (L = alkyl, aryl, N, S, O, etc.) in those complexes, since we often obtain one of $M(\eta\text{-}C_5H_5)_2X_2$ (M = Mo, W; X = Cl, Br, I) compounds as the final product of the reactions commonly used in our thermochemical studies.

Experimental

Calorimeter

The reaction enthalpies and the solution heats were measured in the reaction-solution calorimeter previously described [3]. Some other important details of the experimental technique have also been noted elsewhere [2,3].

Compounds

The $M(\eta\text{-}C_5H_5)_2H_2$ (M = Mo, W) samples were prepared as described by Green et al. [4] and resublimed before use. B.D.H. carbon tetrabromide was also resublimed before use, and B.D.H. bromoform was purified [5] before each experiment. The solvent for the reactions, B.D.H. Analar toluene, was used without any further treatment.

Reactions

The nature of the products of reaction 2 was demonstrated by Green et al. [4]. Using a Perkin-Elmer F 11 Gas Chromatograph we were able to identify the volatile product of reaction 1 as $CHBr_3$.

Results and discussion

The measured enthalpies of reactions 1 and 2 are shown in Tables 1 and 2 respectively

$$Mo(\eta\text{-}C_5H_5)_2H_2\ (c) + 2\ CBr_4(soln) \rightarrow Mo(\eta\text{-}C_5H_5)_2Br_2\ (c) + 2\ CHBr_3(soln) \qquad (1)$$

$$W(\eta\text{-}C_5H_5)_2H_2\ (c) + 2\ CBr_4(soln) \rightarrow W(\eta\text{-}C_5H_5)_2Br_2\ (c) + 2\ CHBr_3(soln) \qquad (2)$$

The value obtained for the heat of solution of CBr_4 in toluene was 8.034 ± 0.032 kJ mol^{-1} (mean of five runs). No dilution heat effects were detected in the working molar range used (in the five runs CBr_4 mass varied from about 2.2 to 5.2 g). The heat of solution of stoichiometric amounts of $CHBr_3$ in solutions of CBr_4 in toluene was —1.74 ± 0.09 kJ mol^{-1} (mean of five runs).

The values of $\Delta H_f^\circ[M(\eta\text{-}C_5H_5)_2Br_2\ (c)]$ and $\bar{D}(M—H) - \bar{D}(M—Br)$, both for molybdenum and tungsten (Table 3) were obtained from the mean values of Tables 1 and 2 and the following auxiliary data (kJ mol^{-1}): $\Delta H_f^\circ[CBr_4\ (c)] = 18.8$ [6]; $\Delta H_f^\circ[CHBr_3\ (l)]$ —28.5 [6]; $\Delta H_f^\circ[Mo(\eta\text{-}C_5H_5)_2H_2\ (c)] = 210.3 \pm 5.8$ [2]; $\Delta H_f^\circ[W(\eta\text{-}C_5H_5)_2H_2\ (c)] = 214.8 \pm 5.0$ [2]; $\Delta H_f^\circ[Br\ (g)] = 111.859 \pm 0.004$ [7]; $\Delta H_f^\circ[H\ (g)] = 217.986 \pm 0.004$ [7]; $\Delta H_s^\circ[M(\eta\text{-}C_5H_5)_2Br_2] - \Delta H_s^\circ[M(\eta\text{-}C_5H_5)_2H_2] = 8.4 \pm 8.4$ (M = Mo, W; estimated values).

The major source of error in the values of Table 3 comes from the enthalpies of formation of carbon tetrabromide and bromoform. The quoted ΔH_f° values seem to be the most reliable, but it is difficult assess their accuracy. For this reason we assigned to their difference uncertainty an interval of ±8.4 kJ mol^{-1}.

If we take $\bar{D}(Mo—H)$ and $\bar{D}(W—H)$ previously derived [2] we obtain $\bar{D}(Mo—Br) = 242.0$ kJ $mol^{-1}$and $\bar{D}(W—Br) = 298.9$ kJ mol^{-1}. In Figure 1 these values are compared with other $\bar{D}(M—L)$ results so far derived. It may be

TABLE 1

REACTION OF $Mo(\eta\text{-}C_5H_5)_2H_2$ (c) WITH CBr_4 IN TOLUENE

$Mo(\eta\text{-}C_5H_5)_2H_2$ mass (g)	CBr_4 mass (g)	ϵ (JK^{-1})	ΔT (K)	$-\Delta H_r$ (kJ mol^{-1})
0.26429	4.06654	250.40	1.4327	309.68
0.19710	2.98797	238.93	1.1584	320.38
0.21786	3.12996	227.77	1.3418	320.04
0.25009	3.66468	245.36	1.4220	318.29
0.23868	4.50658	249.62	1.3055	311.49
Mean $\Delta H_r = -316.0 \pm 4.5$ kJ mol^{-1}				

ϵ = calibration constant; ΔT = measured temperature difference

TABLE 2

REACTION OF $W(\eta\text{-}C_5H_5)_2H_2$ (c) WITH CBr_4 IN TOLUENE

$W(\eta\text{-}C_5H_5)_2H_2$ mass (g)	CBr_4 mass (g)	ϵ (JK^{-1})	ΔT (K)	$-\Delta H_r$ (kJ mol^{-1})
0.29137	3.28241	250.85	1.1827	321.80
0.30226	4.77470	248.28	1.2443	323.04
0.21815	4.69530	251.39	0.8936	325.47
0.22039	3.30406	249.99	0.8901	319.12
0.26214	3.04881	245.43	1.0827	320.36
Mean $\Delta H_r = -322.0 \pm 2.2$ kJ mol^{-1}				

ϵ = calibration constant; ΔT = measured temperature difference

TABLE 3

BOND-ENTHALPY CONTRIBUTION DIFFERENCES

M	ΔH_f^0 [$M(\eta\text{-}C_5H_5)_2Br_2$ (c)] (kJ mol^{-1})	$\bar{D}$(M—H) — $\bar{D}$(M—Br) (kJ mol^{-1})
Mo	8.4 ± (18.3)	9.4 ± (9.7)
W	6.9 ± (17.7)	6.4 ± (9.5)

For explanation of uncertainty intervals see text

noticed that $\bar{D}$(W—L) — $\bar{D}$(Mo—L) differences are relatively constant, varying between 44 and 62 kJ mol^{-1} (mean 53 ± 7 kJ mol^{-1}). This is a common feature in metal—ligand bond energies. On the other hand we note that all values of Figure 1 were based either directly or indirectly on $\bar{D}$(M—Cl) values which

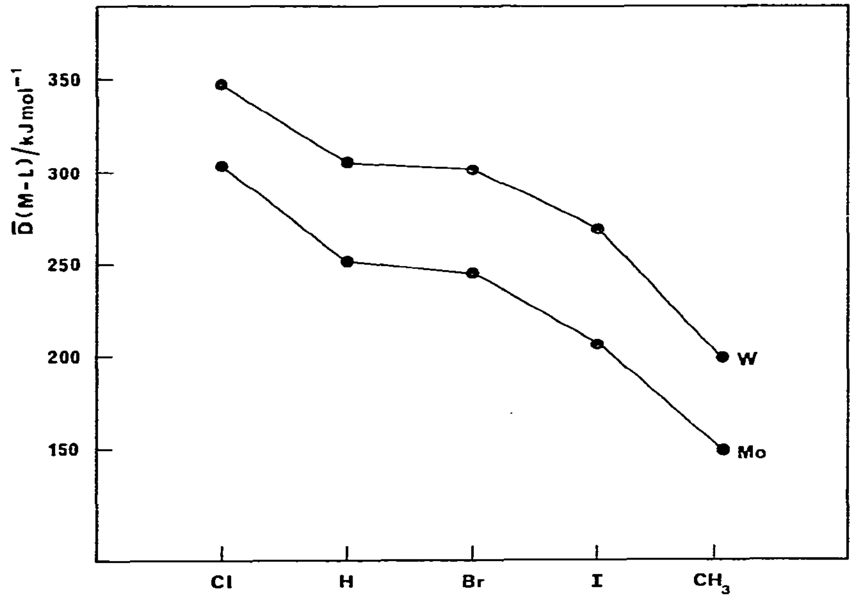

Fig. 1. Bond-enthalpy contributions $\bar{D}$(M—L) in $M(\eta\text{-}C_5H_5)_2L_2$ compounds.

were assumed [8] to be equal to the mean bond dissociation enthalpies in $MoCl_6$ and WCl_6. This assumption can be tested if we compare $\bar{D}$(M—Br) herein derived with $\bar{D}$(M—Br) in MBr_6. Unfortunately the value is available only for tungsten hexabromide; it is 290 kJ mol^{-1}, not very far from 298.9 kJ mol^{-1}.

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References

1 J.C.G. Calado, A.R. Dias, J.A. Martinho Simões and M.A.V. Ribeiro da Silva, J. Chem. Soc. Chem. Commun., (1978) 737.
2 J.C.G. Calado, A.R. Dias, J.A. Martinho Simões and M.A.V. Ribeiro da Silva, J. Organometal. Chem., 174 (1979) 77.
3 J.C.G. Calado, A.R. Dias, J.A. Martinho Simões and M.A.V. Ribeiro da Silva, Rev. Port. Quim., (1979) (in press).
4 M.L.H. Green and P.J. Knowles, J. Chem. Soc. Perkin I, (1973) 989.
5 D.D. Perrin, W.L.F. Armarego and D.R. Perrin, Purification of Laboratory Chemicals, Pergamon Press, New York, 1966.
6 D.D. Wagman, W.H. Evans, V.B. Parker, I. Halow, S.M. Bailey and R.H. Schumm, Nat. Bur. Stand. Tech. Notes, 1—4 (1969) Washington, D.C..
7 J.D. Cox, CATCH Tables, School of Molecular Sciences, University of Sussex, Brighton, 1972.
8 V.I. Tel'noi, I.B. Rabinovich, K.V. Kir'yanov and A.S. Smirnov, Dokl. Akad. Nauk S.S.S.R., 231 (1976) 903.