Enthalpies of Formation of $[Mo(\eta\text{-}C_5H_5)_2(SR)_2]$ Complexes; R = $n\text{-}C_3H_7$, $i\text{-}C_3H_7$, $n\text{-}C_4H_9$, or $t\text{-}C_4H_9$

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The standard enthalpies of formation of the title complexes at 298.15 K have been determined by reaction-solution calorimetry. The results gave $\Delta H_f^\ominus\{[Mo(\eta\text{-}C_5H_5)_2\{S(n\text{-}C_3H_7)\}_2], c\} = 4.6 \pm 5.3$, $\Delta H_f^\ominus\{[Mo(\eta\text{-}C_5H_5)_2\{S(i\text{-}C_3H_7)\}_2], c\} = 57.1 \pm 5.7$, $\Delta H_f^\ominus\{[Mo(\eta\text{-}C_5H_5)_2\{S(n\text{-}C_4H_9)\}_2], c\} = 14.0 \pm 5.7$, and $\Delta H_f^\ominus\{[Mo(\eta\text{-}C_5H_5)_2\{S(t\text{-}C_4H_9)\}_2], c\} = 6.9 \pm 4.4$ kJ mol^{-1}. The metal–sulphur mean bond-enthalpy contributions have been derived as $\bar{D}[Mo\text{–}S(n\text{-}C_3H_7)] \approx 237$, $\bar{D}[Mo\text{–}S(i\text{-}C_3H_7)] \approx 202$, $\bar{D}[Mo\text{–}S(n\text{-}C_4H_9)] \approx 211$, and $\bar{D}[Mo\text{–}S(t\text{-}C_4H_9)] \approx 193$ kJ mol.

MANY complexes containing molybdenum–sulphur bonds are known and some of them are of particular importance as models for biological systems. A knowledge of metal–molybdenum bond strengths should enable a deeper understanding of the reactivity of these systems but such data are not available in the literature and very few other metal–sulphur bond-enthalpy contributions are known.[1]

Having established the value of reaction-solution calorimetry to determine M–L bond-enthalpy contributions in complexes[2] $[M(\eta\text{-}C_5H_5)_2L_2]$ (L = H, Cl, Br, I, CH_3, *etc.*) we have extended our studies to the related dithiolate complexes $[Mo(\eta\text{-}C_5H_5)_2(SR)_2]$, where R = $n\text{-}C_3H_7$, $i\text{-}C_3H_7$, $n\text{-}C_4H_9$, or $t\text{-}C_4H_9$, in order to determine the M–S bond strengths, and the effect of changes in the alkyl groups R.

EXPERIMENTAL

Calorimeter.—The reaction-solution calorimeter and the experimental technique used are described elsewhere.[2b,c] All the compounds involved in the present studies are fairly air-stable, and there was no need to make the thermochemical measurements under a nitrogen atmosphere.

Compounds.—Complexes $[Mo(\eta\text{-}C_5H_5)_2(SR)_2]$ (R = $n\text{-}C_3H_7$, $i\text{-}C_3H_7$, $n\text{-}C_4H_9$, or $t\text{-}C_4H_9$) were prepared and purified as described in the literature.[3] The reaction solutions were prepared from B.D.H. AnalaR hydrochloric acid and Merck *p.a.* acetone, which were used without any further treatment. Compounds $n\text{-}C_4H_9SH$ and $t\text{-}C_4H_9SH$ (Fluka) were dried over CaO and distilled under dry nitrogen; compounds $n\text{-}C_3H_7SH$ and $i\text{-}C_3H_7SH$ (Fluka) were dried over $CaCl_2$ and distilled over dry nitrogen.

Reactions.—Thermochemical measurements of the reactions (1) were used to derive the standard enthalpies of

$$[Mo(\eta\text{-}C_5H_5)_2(SR)_2]\ (c) + 2HCl\ (soln) \longrightarrow [Mo(\eta\text{-}C_5H_5)_2Cl_2]\ (soln) + 2\ RSH\ (soln) \quad (1)$$

formation of $[Mo(\eta\text{-}C_5H_5)_2(SR)_2]$ (c) complexes. With R = $i\text{-}C_3H_7$, $n\text{-}C_4H_9$, or $t\text{-}C_4H_9$, an 8.3 mol dm^{-3} aqueous solution of HCl ensured rapid and complete reaction of the respective complexes. With R = $n\text{-}C_3H_7$ it was necessary to use a 1 : 1 mixture of 8.3 mol dm^{-3} aqueous HCl and acetone. The possible disadvantages of this mixture from a thermochemical point of view, together with some tests performed, were discussed in the preceding paper.[2e]

The products of the reactions were confirmed by i.r. spectroscopic analysis.

All reaction and solution enthalpies presented are mean values from five independent measurements and refer to 298.15 K. The uncertainties quoted are twice the standard deviation of the mean in each case.

Auxiliary Data.—The following standard enthalpies of formation at 298 K were used in evaluating the thermochemical results (values in kJ mol^{-1}): $\Delta H_f^\ominus$[HCl, aq (8.3 mol dm^{-3})] = -156.824 ± 0.004;[4] $\Delta H_f^\ominus\{[Mo(\eta\text{-}C_5H_5)_2Cl_2], c\} = -95.8 \pm 2.5$;[5] $\Delta H_f^\ominus(n\text{-}C_3H_7SH, l) = -99.54 \pm 0.63$;[6] $\Delta H_f^\ominus(i\text{-}C_3H_7SH, l) = -105.52 \pm 0.63$;[6] $\Delta H_f^\ominus(n\text{-}C_4H_9SH, l) = -124.3 \pm 1.2$;[6] $\Delta H_f^\ominus(t\text{-}C_4H_9SH, l) = -140.21 \pm 0.84$;[6] $\Delta H_f^\ominus(n\text{-}C_3H_7S, g) = 99.4 \pm 8.4$; $\Delta H_f^\ominus(i\text{-}C_3H_7S, g) = 91.0 \pm 8.4$; $\Delta H_f^\ominus(n\text{-}C_4H_9S, g) = 79.1 \pm 8.5$; $\Delta H_f^\ominus(t\text{-}C_4H_9S, g) = 57.6 \pm 8.4$; $\Delta H_f^\ominus(Cl, g) = 121.302 \pm 0.008$;[7] $\Delta H_f^\ominus(H, g) = 217.997 \pm 0.006$;[7] a value of -162.47 ± 0.28 for the standard enthalpy of formation of HCl in a 1 : 1 mixture of 8.3 mol dm^{-3} aqueous HCl and acetone was derived in the preceding paper.[2e] The enthalpies of solution of $[Mo(\eta\text{-}C_5H_5)_2Cl_2]$ in 8.3 mol dm^{-3} aqueous HCl and in the above mentioned mixture are 12.9 ± 1.1[2a] kJ mol^{-1} and 2.2 ± 1.1[2e] kJ mol^{-1} respectively. The standard enthalpies of formation of gaseous ˙SR radicals were obtained from $\bar{D}$(alkyl-S–H) = 384.9 ± 8.4[8] kJ mol^{-1} and $\Delta H_f^\ominus(n\text{-}C_3H_7SH, g) = -67.53 \pm 0.67$[6] kJ mol^{-1}, $\Delta H_f^\ominus(i\text{-}C_3H_7SH, g) = -75.90 \pm 0.67$[6] kJ mol^{-1}, $\Delta H_f^\ominus(n\text{-}C_4H_9SH, g) = -87.78 \pm 1.21$[6] kJ mol^{-1}, and $\Delta H_f^\ominus(t\text{-}C_4H_9SH, g) = -109.29 \pm 0.88$[6] kJ mol^{-1}.

RESULTS AND DISCUSSION

The thermochemical results are summarized in Table 1. ΔH_r Refers to the enthalpy of reaction (1), and ΔH_d to the enthalpy of solution of the respective thiol in the calorimetric solution containing stoicheiometric amounts of $[Mo(\eta\text{-}C_5H_5)_2Cl_2]$.

TABLE 1

Thermochemical results (in kJ mol^{-1}) for reactions (1)

$[Mo(\eta\text{-}C_5H_5)_2(SR)_2]$	R = n-C_3H_7	R = i-C_3H_7	R = n-C_4H_9	R = t-C_4H_9
ΔH_r	9.5	−6.58	−10.7	−23.55
	±1.2	±0.78	±1.2	±0.71
ΔH_d	−9.1	15.4	10.6	16.5
	±2.1	±2.4	±2.1	±1.5

The enthalpies of formation of the crystalline and gaseous complexes, together with the estimated enthalpies of sublimation at 298 K, are collected in Table 2. Values of $\Delta H_f^\ominus$ (c) were derived from ΔH_r and ΔH_d values and the auxiliary data already given.

TABLE 2

Enthalpies of formation, ΔH_f° (c) and ΔH_f° (g) (in kJ mol^{-1})

Compound	ΔH_f°(c)	ΔH_s° *	ΔH_f°(g)
$[Mo(\eta\text{-}C_5H_5)_2\{S(n\text{-}C_3H_7)\}_2]$	4.6 ± 5.3	90 ± 10	94.6 ± 11
$[Mo(\eta\text{-}C_5H_5)_2\{S(i\text{-}C_3H_7)\}_2]$	57.1 ± 5.7	90 ± 10	147.1 ± 12
$[Mo(\eta\text{-}C_5H_5)_2\{S(n\text{-}C_4H_9)\}_2]$	14.0 ± 5.7	92 ± 10	106.0 ± 12
$[Mo(\eta\text{-}C_5H_5)_2\{S(t\text{-}C_4H_9)\}_2]$	6.9 ± 4.4	92 ± 10	98.9 ± 11

* Estimated values.

The value of $\Delta H_s^\circ\{[Mo(\eta\text{-}C_5H_5)_2Cl_2]\} = 100.4 \pm 4.2$ [5] kJ mol^{-1} was used to evaluate the mean bond-enthalpy contribution differences (Table 3).* Bond strengths $\bar{D}$(Mo–SR) were obtained assuming $\bar{D}$(Mo–Cl) = 303.8 [5,2d] kJ mol^{-1}. There is a fair agreement between these bond energies and a prediction (*ca.* 200 kJ mol^{-1}) based on a correlation of $\bar{D}$(M–L) values in $[Mo(\eta\text{-}C_5H_5)_2L_2]$ complexes and ligand electronegativities.[2e,2f] Although a smaller difference for $\bar{D}[Mo\text{-}S(n\text{-}C_3H_7)] - \bar{D}[Mo\text{-}S(n\text{-}C_4H_9)]$ than observed was expected, the thermodynamic stabilities of those complexes follow the order of bulkiness of the respective ligands. A rough estimation of ligand cone angles[9] shows that θ values for $i\text{-}C_3H_7S$ and $t\text{-}C_4H_9S$ are *ca.* 18° larger than calculated for $n\text{-}C_3H_7S$ and $n\text{-}C_4H_9S$. The lack of *X*-ray structures for the $[Mo(\eta\text{-}C_5H_5)_2(SR)_2]$ complexes studied prevents further discussion of these steric effects.

TABLE 3

Bond enthalpy contributions (in kJ mol^{-1})

Compound	$\bar{D}$(Mo–Cl) − $\bar{D}$(Mo–SR)	$\bar{D}$(Mo–SR)
$[Mo(\eta\text{-}C_5H_5)_2\{S(n\text{-}C_3H_7)\}_2]$	66.9 ± 10	236.9
$[Mo(\eta\text{-}C_5H_5)_2\{S(i\text{-}C_3H_7)\}_2]$	101.5 ± 10	202.3
$[Mo(\eta\text{-}C_5H_5)_2\{S(n\text{-}C_4H_9)\}_2]$	92.9 ± 10	210.9
$[Mo(\eta\text{-}C_5H_5)_2\{S(t\text{-}C_4H_9)\}_2]$	110.8 ± 10	193.0

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* It was assumed that $\bar{D}(M\text{–}C_5H_5)$ is the same in the complexes studied and in the chloro-complexes. Differences $\bar{D}$(Mo–Cl) − $\bar{D}$(Mo–SR) do not depend upon Tel'noi and Rabinovich's [5] values for the chloro-complexes.

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