The Standard Enthalpies of Formation of Tris(pentane-2,4-dionato)molybdenum(III) and Dioxobis(pentane-2,4-dionato)molybdenum(VI), and the Molybdenum–Pentane-2,4-dionate Bond-enthalpy Contributions

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The standard enthalpies of formation at 298.15 K of the crystalline solids [Mo(pd)$_3$], $\Delta H_f^{\ominus} = -1323.9 \pm 5.9$ kJ mol^{-1}, and [MoO$_2$(pd)$_2$] (pd = pentane-2,4-dionate), $\Delta H_f^{\ominus} = -1\,365.5 \pm 4.5$ kJ mol^{-1}, have been determined using solution reaction calorimetry. The mean Mo–O bond-enthalpy contributions involving the pentane-2,4-dionate groups have been assessed in the two compounds as 192.0 and 187.3 kJ mol^{-1}, respectively.

THE enthalpies of formation of the crystalline tris(pentane-2,4-dionates), [M(pd)$_3$], of Al^{III}, Ga^{III}, Cr^{III}, Mn^{III}, and Fe^{III} were determined by Irving and his coworkers[1] using solution reaction calorimetry. The enthalpies of combustion of [M(pd)$_3$] (M = Al^{III}, Ga^{III}, or In^{III}) measured by Cavell and Pilcher[2] confirmed the corresponding results from reaction calorimetry. Since tris(pentane-2,4-dionato)molybdenum(III) is spontaneously inflammable in air, reaction calorimetry was considered to be the more suitable of these methods for determining the enthalpy of formation of this compound, which is quantitatively hydrolysed and the Mo^{III} oxidised to Mo^{IV} in a strongly acidic solution containing iron(III) chloride. Dioxobis(pentane-2,4-dionato)molybdenum(VI) is quantitatively hydrolysed in an acidic solution. These two compounds were studied to investigate the effect of the difference in the oxidation state of the molybdenum on the bond-enthalpy contributions.

EXPERIMENTAL

The Calorimeter and Auxiliary Equipment.—A glass Dewar calorimeter (capacity 150 cm^3) was used. Reactant samples were sealed in thin glass ampoules which were broken under the solution at the appropriate time by compression between two glass rings: the energy associated with ampoule breaking was found to be <0.05 J. The calorimeter was equipped with a two-bladed glass stirrer; temperatures were recorded to 10^{-4} K at fixed intervals of *ca.* 20 s by a Hewlett–Packard quartz thermometer (HP 2801A) with a digital recorder (HP 562A). The calorimeter was calibrated electrically for each experiment. A constantan resistance of *ca.* 90 Ω was placed in a mercury-filled thin glass tube and the current for this heater was obtained from a stabilised power supply (Farnell C1). The voltage across the heater was measured with a Solartron A210 digital voltmeter and the current was determined from the voltage decrease across a standard 1-Ω resistance. The time for the electrical calibration was controlled by generating 0.1-s square-wave pulses from the 200-kHz Droitwich signal, then switching the current from a dummy heater to the calorimeter heater for a predetermined pulse count. The calorimeter top-plate was sealed to the Dewar with an O ring and an additional gas-entry port was provided so that reactions could be carried out under an inert atmosphere. The calorimeter was submerged in a water thermostat maintained at 25.000 ± 0.001 °C.

Materials.—An analytically pure sample of tris(pentane-2,4-dionato)molybdenum(III) was prepared and purified as described previously;[3] all the subsequent manipulations were performed under an atmosphere of purified nitrogen. Dioxobis(pentane-2,4-dionato)molybdenum(VI), [MoO$_2$(pd)$_2$] (Climax Molybdenum), was recrystallised twice from purified pentane-2,4-dione and final traces of solvent were removed *in vacuo*. Iron(III) chloride (B.D.H., Laboratory reagent) was purified by sublimation *in vacuo*. A Cambrian Chemical sample of FeCl$_2$ of stated minimum purity 99.9% was used. Sodium molybdate, Na$_2$[MoO$_4$] (Alpha Products), was dried at 120 °C before use. B.D.H. AnalaR sodium chloride was used. Pentane-2,4-dione (Hpd) was purified by fractional distillation at atmospheric pressure; the sample was freshly distilled before each experiment. Constant-boiling hydrochloric acid of composition HCl·7.97H$_2$O was used as a reagent.

For the hydrolysis and oxidation reactions the solvents were degassed and saturated with purified nitrogen before insertion in the calorimeter.

RESULTS AND DISCUSSION

The thermochemical reaction for determining the enthalpy of formation of [Mo(pd)$_3$] was (1). The

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[1] J. O. Hill and R. J. Irving, *J. Chem. Soc.* (*A*), 1966, 971; 1967, 1413; 1968, 1052, 3116; R. J. Irving and G. W. Walter, *J. Chem. Soc.* (*A*), 1969, 2690.

[2] K. J. Cavell and G. Pilcher, *J.C.S. Faraday I*, 1977, 1590.

[3] T. G. Dunne and F. A. Cotton, *Inorg. Chem.*, 1963, **2**, 263.

standard enthalpy of this reaction was determined by measuring the enthalpy of solution of each reactant and

$$[Mo(pd)_3](c) + 3FeCl_3(c) + 4H_2O(l) + 2NaCl(c) \longrightarrow Na_2[MoO_4](c) + 3FeCl_2(c) + 5HCl \text{ (in 7.97 } H_2O)(l) + 3Hpd(l) \quad (1)$$

product in the calorimetric solvent, so that the final solution resulting from the dissolution of all the reactants was of the same composition as the corresponding solution from the dissolution of all the products. Since the HCl was added as $HCl{\cdot}7.97H_2O(l)$ a minor adjustment in the water content of the initial solvent for dissolution of the reactants was made to ensure identity of the two final solutions; this was checked using u.v. spectra. The initial solvent was of the composition $FeCl_3 : HCl : HClO_4 : H_2O$ in the molar ratio 1 : 15 : 30 : 1 000.

TABLE 1

Determination of $\Delta H_f^\ominus$ [$Mo(pd)_3$, c, 298.15 K]

Reaction		Number of experiments	ΔH (298 K)/kJ mol^{-1}
$H_2O(l)$ + solvent	= solution A_1	4	$\Delta H_1 = -0.05 \pm 0.00$
$NaCl(c)$ + solution A_1	= solution A_2	5	$\Delta H_2 = 5.27 \pm 0.05$
$FeCl_3(c)$ + solution A_2	= solution A_3	5	$\Delta H_3 = -117.46 \pm 0.37$
$[Mo(pd)_3](c)$ + solution A_3	= solution F	4	$\Delta H_4 = -12.41 \pm 0.52$
$HCl{\cdot}7.97H_2O(l)$ + solvent	= solution B_1	4	$\Delta H_5 = -2.52 \pm 0.01$
$Hpd(l)$ + solution B_1	= solution B_2	3	$\Delta H_6 = -1.08 \pm 0.05$
$FeCl_2(c)$ + solution B_2	= solution B_3	5	$\Delta H_7 = -69.43 \pm 0.15$
$Na_2[MoO_4](c)$ + solution B_3	= solution F	5	$\Delta H_8 = -53.62 \pm 0.69$

The results are summarised in Table 1 where, in accordance with normal thermochemical practice, the errors assigned are uncertainty intervals,[4] *i.e.* twice the standard deviation of the mean. The enthalpy of reaction (1) is given by (2).

TABLE 2

Determination of $\Delta H_f^\ominus$ [$MoO_2(pd)_2$, c, 298.15 K]

Reaction		Number of experiments	ΔH (298 K)/kJ mol^{-1}
$H_2O(l)$ + solvent	= solution A_1	5	$\Delta H_1 = -1.68 \pm 0.04$
$NaCl(c)$ + solution A_1	= solution A_2	5	$\Delta H_2 = 2.60 \pm 0.05$
$[MoO_2(pd)_2](c)$ + solution A_2	= solution F	4	$\Delta H_3 = 42.64 \pm 0.25$
$HCl{\cdot}7.97H_2O(l)$ + solvent	= solution B_1	4	$\Delta H_4 = -27.36 \pm 0.21$
$Hpd(l)$ + solution B_1	= solution B_2	4	$\Delta H_5 = 4.75 \pm 0.02$
$Na_2[MoO_4](c)$ + solution B_2	= solution F	4	$\Delta H_6 = -34.26 \pm 0.37$

$$\Delta H_r^\ominus(1) = 4\Delta H_1 + 2\Delta H_2 + 3\Delta H_3 + \Delta H_4 - 5\Delta H_5 - 3\Delta H_6 - 3\Delta H_7 - \Delta H_8 = -76.7 \pm 1.5 \text{ kJ mol}^{-1} \quad (2)$$

The value $\Delta H_f^\ominus$ [$Mo(pd)_3$, c, 298.15 K] = −1 323.9 ± 5.9 kJ mol^{-1} was obtained using the following auxiliary data (in kJ mol^{-1}) at 298 K: $\Delta H_f^\ominus(Na_2[MoO_4]$, c) = −1 467.6 ± 3.3,[5] $\Delta H_f^\ominus$(NaCl, c) = −411.00 ± 0.01,[6] $\Delta H_f^\ominus(HCl{\cdot}7.97H_2O$, l) = −160.00 ± 0.01,[6] $\Delta H_f^\ominus(H_2O$, l) = −285.83 ± 0.01,[7] $\Delta H_f^\ominus$(Hpd, l) = −423.8 ± 1.5,[8] and $\Delta H_f^\ominus(FeCl_3$, c) − $\Delta H_f^\ominus(FeCl_2$, c) = −57.70 ± 0.46.[9]

The thermochemical reaction for determining the enthalpy of formation of $[MoO_2(pd)_2]$ was (3). The hydrolysis of $[MoO_2(pd)_2]$ in an aqueous acidic solvent was found to be too slow for calorimetric measurement, but was rapid in dimethylformamide–perchloric acid–water (70 : 10 : 20). The standard enthalpy of reaction was determined in a manner similar to that used for $[Mo(pd)_3]$ and the results are summarised in Table

$$[MoO_2(pd)_2] \text{ (c)} + 2NaCl \text{ (c)} + 2H_2O \text{ (l)} \longrightarrow Na_2[MoO_4] \text{ (c)} + 2Hpd \text{ (l)} + 2HCl \text{ (in } 7.97H_2O) \text{ (l)} \quad (3)$$

2. Here $\Delta_r H^\ominus(3) = 2\Delta H_1 + 2\Delta H_2 + \Delta H_3 - 2\Delta H_4 - 2\Delta H_5 - \Delta H_6$ = 124.0 ± 0.6 kJ mol^{-1} and $\Delta H_f^\ominus$ [$MoO_2(pd)_2$, c, 298.15 K] = −1 365.5 ± 4.5 kJ mol^{-1}.

The Mean Molybdenum–Oxygen Bond-enthalpy Contributions.—The compound $[MoO_2(pd)_2]$ (c) is comprised of discrete molecules which possess a *cis* arrangement of the oxo-groups in a distorted octahedron of oxygen atoms about the metal centre. The Mo–O(oxo) bonds are of length 1.69 Å and Mo–O(pd) is 1.98 Å for the oxygen atoms *cis* to both oxo-groups and 2.19 Å for the oxygen atoms *trans* to one and *cis* to the other oxo-group. Variable-temperature ^1H n.m.r. studies have shown that $[MoO_2(pd)_2]$ is stereochemically non-rigid in solution but the nature of the molecular rearrangements have not been determined.[10] No structural details are available for $[Mo(pd)_3]$; the only other pentane-2,4-dionatomolybdenum compounds for which structural information has been reported are $[Mo(\eta\text{-}C_7H_7)(pd)(OH_2)][BF_4]$ and

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[4] F. D. Rossini, 'Experimental Thermochemistry,' Interscience, New York, 1956, vol. 1, ch. 14.

[5] D. S. Barnes, 'CATCH Tables, Cr, Mo, and W Compounds,' University of Sussex, 1974.

[6] 'Selected Values of Chemical Thermodynamic Properties,' Nat. Bur. Stand. Tech. Note 270-3, Washington, D.C., 1968.

[7] CODATA, *J. Chem. Thermodynamics*, 1971, **3**, 1.

[8] G. R. Nicholson, *J. Chem. Soc.*, 1957, 2431.

[9] M. F. Koehler and J. P. Coughlin, *J. Phys. Chem.*, 1959, **63**, 605.

[10] B. M. Craven, K. C. Ramey, and W. B. Wise, *Inorg. Chem.*, 1971, **10**, 2626.

$[Mo(\eta\text{-}C_7H_7)(pd)(NCS)]$, the former containing Mo–O bonds of length 2.085 Å.[11] The compound $[Mo(pd)_3]$ is expected [3] to contain an essentially octahedral arrangement of oxygen atoms about the metal centre to give a molecular unit of D_3 symmetry.

The mean Mo–O bond-enthalpy contribution in $[Mo(pd)_3]$ may be defined as one sixth of the enthalpy of the disruption reaction (4) so that we obtain expression (5). Application of this equation requires $\Delta H_{sub}^{\ominus}$

$$[Mo(pd)_3](g) \longrightarrow Mo(g) + 3pd(g) \qquad (4)$$

$$\bar{D}(Mo\text{–}O) = \tfrac{1}{6}\{\Delta H_f^{\ominus}(Mo,\,g) + 3\Delta H_f^{\ominus}(pd,\,g) - \Delta H_f^{\ominus}[Mo(pd)_3,\,g]\} \qquad (5)$$

$[Mo(pd)_3,\,c]$; since no experimental value is available it is assumed that this will be the same as that reported [12] for $[Cr(pd)_3]$, 123 ± 3 kJ mol^{-1}. With $\Delta H_f^{\ominus}(Mo,g) = 658.1 \pm 2.1$ kJ mol^{-1} (ref. 5) and $\Delta H_f^{\ominus}(pd,\,g) = -235.7$ kJ mol^{-1} as estimated by Cavell and Pilcher,[2] $\Delta H^{\ominus}$ (disruption) = 1 151.9 kJ mol^{-1} and $\bar{D}(Mo\text{–}O) = 192.0$ kJ mol^{-1}.

The enthalpy of disruption of $[MoO_2(pd)_2]$ according to equation (6) is calculated to be 1 927.5 kJ mol^{-1} assuming $\Delta H_{sub}^{\ominus}[MoO_2(pd)_3,\,c]$ to be the same as for $[Mo(pd)_3]$ and

$$[MoO_2(pd)_2](g) \longrightarrow Mo(g) + 2O(g) + 2pd(g) \qquad (6)$$

$\Delta H_f^{\ominus}(O,\,g) = 249.17 \pm 0.10$ kJ mol^{-1}. This enthalpy of disruption may be divided into two bond-enthalpy contributions as in (7). To obtain $\bar{D}[Mo\text{–}O(pd)]$ it is

$$\Delta H^{\ominus}(\text{disruption}) = 2\bar{D}[Mo\text{–}O(oxo)] + 4\bar{D}(Mo\text{–}O(pd)] \qquad (7)$$

necessary to assume a value for $\bar{D}[Mo\text{–}O(oxo)]$. The simplest assumption would be that $\bar{D}[Mo\text{–}O(oxo)]$ equals $\bar{D}(Mo\text{–}O)$ in MoO_3, calculated from $\Delta H_f^{\ominus}(MoO_3,\,g) = -361.6 \pm 4.1$ kJ mol^{-1},[5] *i.e.* $\bar{D}(Mo\text{–}O) = 589.1$ kJ mol^{-1}. Also $\bar{D}(Mo\text{–}O)$ in MoO_2 may be calculated from $\Delta H_f^{\ominus}(MoO_2,\,g) = -14 \pm 41$ kJ mol^{-1},[5] *i.e.* $\bar{D}(Mo\text{–}O) = 585$ kJ mol^{-1}, close to the value in MoO_3 although the oxidation state of Mo is different.

Accepting $\bar{D}[Mo\text{–}O(oxo)] = 589.1$ kJ mol^{-1}, then $\bar{D}[Mo\text{–}O(pd)]$ in $[MoO_2(pd)_2] = 187.3$ kJ mol^{-1}. Uncertainties in the two values of $\bar{D}[Mo\text{–}O(pd)]$ arise from (*a*) the estimations of $\Delta H_{sub}^{\ominus}$, but these do not have a large effect since only $\frac{1}{6}\,\Delta H_{sub}^{\ominus}\,[Mo(pd)_3,\,c]$ enters into $\bar{D}[Mo\text{–}O(pd)]$ in $[Mo(pd)_3]$; (*b*) the assumption of the transferability of $\bar{D}[Mo\text{–}O(oxo)]$ between MoO_3 and $[MoO_2(pd)_2]$ which could cause a significant uncertainty. Although transferability of bond-enthalpy contributions is well established for organic compounds this is not the case for inorganic compounds. The thermochemical studies reported here are taken to indicate that the average Mo–O bond-enthalpy contribution for the binding of pentane-2,4-dionate to a *cis*-dioxomolybdenum(VI) centre is probably similar to that corresponding to the binding of this ligand to Mo^{III}.

The mean Cr–O bond-enthalpy contribution in $[Cr(pd)_3]$ is calculated from $\Delta H_f^{\ominus}[Cr(pd)_3,\,c] = -1\,533.0 \pm 5.0$ kJ mol^{-1} (ref. 1) to be $\bar{D}(Cr\text{–}O) = 183.3$ kJ mol^{-1}. $\bar{D}(Mo\text{–}O)$ is expected to be greater than $\bar{D}(Cr\text{–}O)$ but the increase of *ca.* 10 kJ mol^{-1} is smaller than that normally observed, *e.g.* for the hexacarbonyls [13] the corresponding increase is *ca.* 40 kJ mol^{-1}.

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