

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 $[\text{Mo}(\text{pd})_3]$, $\Delta H_f^\circ = -1323.9 \pm 5.9 \text{ kJ mol}^{-1}$, and $[\text{MoO}_2(\text{pd})_2]$ (pd = pentane-2,4-dionate), $\Delta H_f^\circ = -1365.5 \pm 4.5 \text{ kJ mol}^{-1}$, 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), $[\text{M}(\text{pd})_3]$, of Al^{III} , Ga^{III} , Cr^{III} , Mn^{III} , and Fe^{III} were determined by Irving and his co-workers¹ using solution reaction calorimetry. The enthalpies of combustion of $[\text{M}(\text{pd})_3]$ ($\text{M} = \text{Al}^{\text{III}}$, Ga^{III} , or In^{III}) measured by Cavell and Pilcher² 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 $<0.05 \text{ J}$. 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 $25.000 \pm 0.001 \text{ }^\circ\text{C}$.

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), $[\text{MoO}_2(\text{pd})_2]$ (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, $\text{Na}_2[\text{MoO}_4]$ (Alpha Products), was dried at $120 \text{ }^\circ\text{C}$ 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 $\text{HCl} \cdot 7.97\text{H}_2\text{O}$ 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

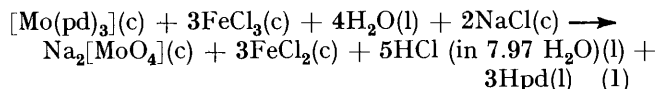
The thermochemical reaction for determining the enthalpy of formation of $[\text{Mo}(\text{pd})_3]$ was (1). The

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



product in the calorimetric solvent, so that the final solution resulting from the dissolution of all the reactants

l) = -285.83 ± 0.01 ,⁷ $\Delta H_f^\ominus(\text{Hpd}, \text{l}) = -423.8 \pm 1.5$,⁸ and $\Delta H_f^\ominus(\text{FeCl}_3, \text{c}) - \Delta H_f^\ominus(\text{FeCl}_2, \text{c}) = -57.70 \pm 0.46$.⁹

The thermochemical reaction for determining the enthalpy of formation of $[\text{MoO}_2(\text{pd})_2]$ was (3). The hydrolysis of $[\text{MoO}_2(\text{pd})_2]$ 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

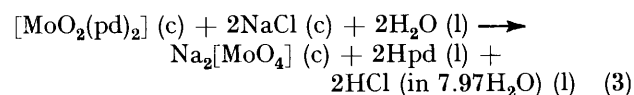
TABLE 1
Determination of ΔH_f^\ominus $[\text{Mo}(\text{pd})_3, \text{c}, 298.15 \text{ K}]$

| Reaction | Number of experiments | ΔH (298 K)/kJ mol ⁻¹ |
|--|-----------------------|---|
| H ₂ O(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 | $\Delta H_3 = -117.46 \pm 0.37$ |
| $[\text{Mo}(\text{pd})_3](\text{c}) + \text{solution A}_3 = \text{solution F}$ | 4 | $\Delta H_4 = -12.41 \pm 0.52$ |
| HCl·7.97H ₂ O(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 | $\Delta H_8 = -53.62 \pm 0.69$ |

was of the same composition as the corresponding solution from the dissolution of all the products. Since the HCl was added as HCl·7.97H₂O(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 FeCl₃:HCl:HClO₄:H₂O in the molar ratio 1:15:30:1 000.

The results are summarised in Table 1 where, in accordance with normal thermochemical practice, the

reaction was determined in a manner similar to that used for $[\text{Mo}(\text{pd})_3]$ and the results are summarised in Table



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

The Mean Molybdenum-Oxygen Bond-enthalpy Contributions.—The compound $[\text{MoO}_2(\text{pd})_2](\text{c})$ is comprised

TABLE 2
Determination of ΔH_f^\ominus $[\text{MoO}_2(\text{pd})_2, \text{c}, 298.15 \text{ K}]$

| Reaction | Number of experiments | ΔH (298 K)/kJ mol ⁻¹ |
|---|-----------------------|---|
| H ₂ O(l) + solvent = solution A ₁ | 5 | $\Delta H_1 = -1.68 \pm 0.04$ |
| NaCl(c) + solution A ₁ = solution A ₂ | 5 | $\Delta H_2 = 2.60 \pm 0.05$ |
| $[\text{MoO}_2(\text{pd})_2](\text{c}) + \text{solution A}_2 = \text{solution F}$ | 4 | $\Delta H_3 = 42.64 \pm 0.25$ |
| HCl·7.97H ₂ O(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 | $\Delta H_6 = -34.26 \pm 0.37$ |

errors assigned are uncertainty intervals,⁴ *i.e.* twice the standard deviation of the mean. The enthalpy of reaction (1) is given by (2).

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

The value ΔH_f^\ominus $[\text{Mo}(\text{pd})_3, \text{c}, 298.15 \text{ K}] = -1 323.9 \pm 5.9 \text{ kJ mol}^{-1}$ was obtained using the following auxiliary data (in kJ mol⁻¹) at 298 K: $\Delta H_f^\ominus(\text{Na}_2[\text{MoO}_4], \text{c}) = -1 467.6 \pm 3.3$,⁵ $\Delta H_f^\ominus(\text{NaCl}, \text{c}) = -411.00 \pm 0.01$,⁶ $\Delta H_f^\ominus(\text{HCl} \cdot 7.97\text{H}_2\text{O}, \text{l}) = -160.00 \pm 0.01$,⁶ $\Delta H_f^\ominus(\text{H}_2\text{O},$

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.

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 $[\text{MoO}_2(\text{pd})_2]$ is stereochemically non-rigid in solution but the nature of the molecular rearrangements have not been determined.¹⁰ No structural details are available for $[\text{Mo}(\text{pd})_3]$; the only other pentane-2,4-dionatomolybdenum compounds for which structural information has been reported are $[\text{Mo}(\eta\text{-C}_7\text{H}_7)(\text{pd})(\text{OH}_2)][\text{BF}_4]$ and

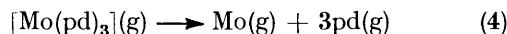
⁸ G. R. Nicholson, *J. Chem. Soc.*, 1957, 2431.

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(η -C₇H₇)(pd)(NCS)], the former containing Mo-O bonds of length 2.085 Å.¹¹ The compound [Mo(pd)₃] is expected³ to contain an essentially octahedral arrangement of oxygen atoms about the metal centre to give a molecular unit of D₃ symmetry.

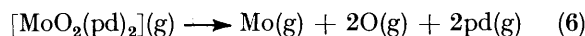
The mean Mo-O bond-enthalpy contribution in [Mo(pd)₃] may be defined as one sixth of the enthalpy of the disruption reaction (4) so that we obtain expression (5). Application of this equation requires $\Delta H_{\text{sub}}^\circ$



$$\bar{D}(\text{Mo-O}) = \frac{1}{6}\{\Delta H_f^\circ(\text{Mo}, \text{g}) + 3\Delta H_f^\circ(\text{pd}, \text{g}) - \Delta H_f^\circ[\text{Mo}(\text{pd})_3, \text{g}]\} \quad (5)$$

[Mo(pd)₃, c]; since no experimental value is available it is assumed that this will be the same as that reported¹² for [Cr(pd)₃], 123 ± 3 kJ mol⁻¹. With $\Delta H_f^\circ(\text{Mo}, \text{g}) = 658.1 \pm 2.1$ kJ mol⁻¹ (ref. 5) and $\Delta H_f^\circ(\text{pd}, \text{g}) = -235.7$ kJ mol⁻¹ as estimated by Cavell and Pilcher,² ΔH° (disruption) = 1151.9 kJ mol⁻¹ and $\bar{D}(\text{Mo-O}) = 192.0$ kJ mol⁻¹.

The enthalpy of disruption of [MoO₂(pd)₂] according to equation (6) is calculated to be 1927.5 kJ mol⁻¹ assuming $\Delta H_{\text{sub}}^\circ[\text{MoO}_2(\text{pd})_2, \text{c}]$ to be the same as for [Mo(pd)₃] and



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

$$2\bar{D}[\text{Mo-O}(\text{oxo})] + 4\bar{D}[\text{Mo-O}(\text{pd})] \quad (7)$$

necessary to assume a value for $\bar{D}[\text{Mo-O}(\text{oxo})]$. The simplest assumption would be that $\bar{D}[\text{Mo-O}(\text{oxo})]$ equals

¹¹ M. Bochman, M. Cooke, M. Green, H. P. Kirsch, F. G. A. Stone, and A. J. Welch, *J.C.S. Chem. Comm.*, 1976, 381.

$\bar{D}(\text{Mo-O})$ in MoO₃, calculated from $\Delta H_f^\circ(\text{MoO}_3, \text{g}) = -361.6 \pm 4.1$ kJ mol⁻¹,⁵ *i.e.* $\bar{D}(\text{Mo-O}) = 589.1$ kJ mol⁻¹. Also $\bar{D}(\text{Mo-O})$ in MoO₂ may be calculated from $\Delta H_f^\circ(\text{MoO}_2, \text{g}) = -14 \pm 41$ kJ mol⁻¹,⁵ *i.e.* $\bar{D}(\text{Mo-O}) = 585$ kJ mol⁻¹, close to the value in MoO₃ although the oxidation state of Mo is different.

Accepting $\bar{D}[\text{Mo-O}(\text{oxo})] = 589.1$ kJ mol⁻¹, then $\bar{D}[\text{Mo-O}(\text{pd})]$ in [MoO₂(pd)₂] = 187.3 kJ mol⁻¹. Uncertainties in the two values of $\bar{D}[\text{Mo-O}(\text{pd})]$ arise from (a) the estimations of $\Delta H_{\text{sub}}^\circ$, but these do not have a large effect since only $\frac{1}{6} \Delta H_{\text{sub}}^\circ[\text{Mo}(\text{pd})_3, \text{c}]$ enters into $\bar{D}[\text{Mo-O}(\text{pd})]$ in [Mo(pd)₃]; (b) the assumption of the transferability of $\bar{D}[\text{Mo-O}(\text{oxo})]$ between MoO₃ and [MoO₂(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 $\Delta H_f^\circ[\text{Cr}(\text{pd})_3, \text{c}] = -1533.0 \pm 5.0$ kJ mol⁻¹ (ref. 1) to be $\bar{D}(\text{Cr-O}) = 183.3$ kJ mol⁻¹. $\bar{D}(\text{Mo-O})$ is expected to be greater than $\bar{D}(\text{Cr-O})$ but the increase of *ca.* 10 kJ mol⁻¹ is smaller than that normally observed, *e.g.* for the hexacarbonyls¹³ the corresponding increase is *ca.* 40 kJ mol⁻¹.

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¹² R. A. Schulz, University of Surrey, personal communication.

¹³ G. Pilcher, M. J. Ware, and D. A. Pittam, *J. Less-Common Metals*, 1975, **42**, 223.