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STANDARD ENTHALPIES OF FORMATION OF THE PENTANE-2,4-DIONATE AND 8-HYDROXYQUINOLATE COMPLEXES OF VANADIUM(III) AND OF OXOVANADIUM(IV) BY SOLUTION-REACTION CALORIMETRY

E.H. JAMEA and G. PILCHER

Department of Chemistry, University of Manchester, Manchester M13 9PL (Gt. Britain)

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ABSTRACT

The standard enthalpies of formation at 298.15 K of the pentane-2,4-dione (Hpd) and 8-hydroxyquinoline (Hox) crystalline complexes of vanadium(III) and oxovanadium(IV) were determined by solution-reaction calorimetry.

$\Delta_f H^0_m(\mathrm{V(pd)_3, c})\ (\mathrm{kJ\ mol^{-1}}) = -1522.8 \pm 4.5$

$\Delta_f H^0_m(\mathrm{V(ox)_3, c})\ (\mathrm{kJ\ mol^{-1}}) = -452.7 \pm 4.5$

$\Delta_f H^0_m(\mathrm{VO(pd)_2, c})\ (\mathrm{kJ\ mol^{-1}}) = -1366.6 \pm 7.6$

$\Delta_f H^0_m(\mathrm{VO(ox)_2, c})\ (\mathrm{kJ\ mol^{-1}}) = -643.5 \pm 7.8$

The enthalpy of sublimation of $\mathrm{VO(pd)_2}$ at 298.15 K, determined using microcalorimetry, was 140.4 ± 1.1 kJ mol^{-1}. The mean bond dissociation enthalpy, $\bar{D}(\mathrm{V{-}O})_{\mathrm{pd}}$, in $\mathrm{V(pd)_3}$ correlated with corresponding values in other $\mathrm{M(pd)_3}$ complexes. $\bar{D}$(M–ligand) is greater in $\mathrm{VOL_2}$ than in $\mathrm{VL_3}$ showing that trends in $\bar{D}$(M–L) in ML_n complexes primarily depend on the number of ligands and not on the oxidation state of M.

INTRODUCTION

Pentane-2,4-dione (written in this paper as Hpd) and 8-hydroxyquinoline (written as Hox) form complexes with virtually every metal in the Periodic Table, hence, thermochemical study of these complexes permits consideration of trends in metal–ligand bond strengths. The first thermochemical studies of pentane-2,4-dionate complexes were made by Jones et al. [1,2] for a series of transition metal complexes, including those of vanadium, using static-bomb calorimetry. Unfortunately, these pioneering studies were made before the difficulties inherent in the combustion technique were properly understood and these early results have been shown to be unreliable. The solution-reaction calorimetric method has proved to be reliable for determining enthalpies of formation of pentane-2,4-dionate complexes [3] and was used previously for a series of 8-hydroxyquinolate complexes [4]. In this

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paper, using the solution-reaction calorimetric method, $\Delta_f H_m^0(V(pd)_3, c)$ and $\Delta_f H_m^0(VO(pd)_2, c)$ were re-examined, and for the first time, $\Delta_f H_m^0(V(ox)_3, c)$ and $\Delta_f H_m^0(VO(ox)_2, c)$ were determined. The enthalpy of sublimation of $VO(pd)_2$ was measured using microcalorimetry but this method was not successful for the other complexes and estimates were required to derive the enthalpies of formation in the gaseous state from which the mean metal–ligand dissociation enthalpies were derived.

EXPERIMENTAL

Materials

$V(pd)_3$ and $VO(pd)_2$ (Alpha Chemical Co.) were used as supplied: microanalyses: $V(pd)_3$, found: C, 51.7; H, 6.0%; expected: C, 51.7; H, 6.1%; $VO(pd)_2$, found: C, 44.7; H, 5.2%; expected: C, 45.3; H, 5.3%. $V(ox)_3$ (99.92 ± 0.10%) was prepared from an aqueous solution of VCl_3 and $VO(ox)_2$ (99.98 ± 0.10%) from an aqueous solution of $VOCl_2$ using the conditions for precipitation as in quantitative analysis [5]. The oxine complexes were dried in air at 400 K and were analysed by hydrolysis in acid followed by titration of the liberated 8-hydroxyquinoline with standard potassium bromate solution. VCl_3 (Alpha Chemical Co.) on the basis of Cl analysis was 98.37% pure, and the observed enthalpy of solution was corrected assuming the impurity to be inert. Pentane-2,4-dione (BDH AnalaR) was purified by fractional distillation, 8-hydroxyquinoline (BDH AnalaR) was used. The calorimetric solvent was constant-boiling hydrochloric acid of composition $HCl \cdot 7.97H_2O$.

Solution-reaction calorimeter

The calorimeter, auxiliary equipment and tests of the accuracy of its performance were reported recently [4].

RESULTS

$V(pd)_3$ and $V(ox)_3$ both hydrolyse rapidly and quantitatively in aqueous hydrochloric acid making feasible the determination of the enthalpy of the thermochemical reaction

$$VL_3(c) + 3HCl \cdot 7.97H_2O(l) = VCl_3(c) + 3HL(c/l) + 23.91H_2O(l)$$

with L = pd or ox.

The standard enthalpy of the thermochemical reaction was determined by measuring (or, where appropriate, calculating from tabulated thermochem-

TABLE 1

Molar enthalpies of solution and reaction at 298.15 K

i	Reactant	Solvent	Solution	No. of expts.	$\Delta_i H_m$ (kJ mol^{-1})
1	$V(pd)_3(c)$	$HCl \cdot 7.97H_2O$	F	5	13.25 ± 0.33
2	$H_2O(l)$	$HCl \cdot 7.97H_2O$	A1	–	-0.66 ± 0.02
3	Hpd(l)	A1	A2	5	-2.92 ± 0.06
4	$VCl_3(c)$	A2	F	4	-107.28 ± 2.51
5	$V(ox)_3(c)$	$HCl \cdot 7.97H_2O$	F1	4	-88.78 ± 0.04
6	Hox(c)	A1	A3	4	-18.24 ± 0.14
7	$VCl_3(c)$	A3	F1	4	-107.31 ± 0.85
8	$VO(pd)_2(c)$	$HCl \cdot 7.97H_2O$	A4	4	11.30 ± 0.70
9	$VO(ox)_2(c)$	$HCl \cdot 7.97H_2O$	A5	4	-64.46 ± 0.12

ical data) the enthalpies of solution of the reactants and products successively in the initial calorimetric solvent so that the final solution resulting from dissolution of all the reactants was of the same composition as that from dissolution of all the products. The results are summarised in Table 1, where, in accordance with normal thermochemical practice, the errors given are uncertainty intervals, i.e., twice the standard deviation of the mean. The relative atomic masses used were those recommended by IUPAC [6]. For the thermochemical reaction

$$V(pd)_3(c) + 3HCl \cdot 7.97H_2O(l) = VCl_3(c) + 3Hpd(l) + 23.91H_2O(l)$$

$$\Delta_r H_m^0 = \Delta_1 H_m - 23.91\Delta_2 H_m - 3\Delta_3 H_m - \Delta_4 H_m$$

$$= 145.1 \pm 2.6 \text{ kJ mol}^{-1}$$

and for

$$V(ox)_3(c) + 3HCl \cdot 7.97H_2O(l) = VCL_3(c) + 3Hox(c) + 23.91H_2O(l)$$

$$\Delta_r H_m^0 = \Delta_5 H_m - 23.91\Delta_2 H_m - 3\Delta_6 H_m - \Delta_7 H_m$$

$$= 89.0 \pm 1.1 \text{ kJ mol}^{-1}$$

With the following auxiliary data, $\Delta_f H_m^0$ (kJ mol^{-1}): $VCl_3(c)$, -581.2 ± 2.1 [7]; Hpd(l), -425.5 ± 1.0 [8]; Hox(c), -87.5 ± 1.3 [9]; HCl in $7.97H_2O(l)$, -160.00 ± 0.01 [7], then

$$\Delta_f H_m^0(V(pd)_3, c) = -1522.8 \pm 4.5 \text{ kJ mol}^{-1}$$

$$\Delta_f H_m^0(V(ox)_3, c) = -452.7 \pm 4.5 \text{ kJ mol}^{-1}$$

$VO(pd)_2$ and $VO(ox)_2$ also hydrolyse rapidly in aqueous hydrochloric acid, and the mean values of the enthalpies of hydrolysis are given in Table 1. The required enthalpies of formation could not be derived in a manner analogous to that used for the VL_3 complexes, because there is no satisfactory V(IV) compound to which these enthalpies of formation could be related. The enthalpies of formation can be determined using the following reactions

$$\mathrm{VO(pd)_2(c) + 2HCl\cdot 7.97H_2O(l) = VO^{2+}(soln.) + 2Cl^-(soln.)}$$
$$\mathrm{+ 2Hpd(l) + 15.94H_2O(l)}$$
$$\Delta_r H^0_m = \Delta_8 H_m - 15.94\Delta_2 H_m - 2\Delta_3 H_m$$
$$= 27.7 \pm 1.4\ \mathrm{kJ\ mol^{-1}}$$

and

$$\mathrm{VO(ox)_2(c) + 2HCl\cdot 7.97H_2O(l) = VO^{2+}(soln.) + 2Cl^-(soln.)}$$
$$\mathrm{+ 2Hox(c) + 15.94H_2O(l)}$$
$$\Delta_r H^0_m = \Delta_9 H_m - 15.94\Delta_2 H_m - 2\Delta_6 H_m$$
$$= -19.4 \pm 0.4\ \mathrm{kJ\ mol^{-1}}$$

With $\Delta_f H^0_m(\mathrm{VO^{2+}}, \mathrm{aq}) = -487.9 \pm 2.9$ kJ mol^{-1} [7] and $\Delta_f H^0_m(\mathrm{Cl^-}$ in $\mathrm{HCl\cdot 7.97H_2O})$ to be the same as for HCl in $7.97\mathrm{H_2O}$, then

$$\Delta_f H^0_m(\mathrm{VO(pd)_2, c}) = -1366.6 \pm 7.6\ \mathrm{kJ\ mol^{-1}}$$
$$\Delta_f H^0_m(\mathrm{VO(ox)_2, c}) = -643.5 \pm 7.8\ \mathrm{kJ\ mol^{-1}}$$

The systematic error arising from the assumption that $\Delta_f H^0_m(\mathrm{VO^{2+}}$ in $\mathrm{HCl\cdot 7.97\ H_2O})$ is equal to the standard-state value in water is unlikely to be large because Bertrand et al. [10] observed that the enthalpy of the reaction

$$\mathrm{Fe^{2+}(soln.) + VO_2^+(soln.) + 2H^+(soln.)}$$
$$\mathrm{= Fe^{3+}(soln.) + VO^{2+}(soln.) + H_2O(l)}$$

was independent of acid concentration in the range 0.1–0.6 mol l^{-1}. The conditions used in this work, however, were outside this range and the derived uncertainties for $\Delta_f H^0_m(\mathrm{VOL_2, c})$ have been doubled to include the effect of this unknown systematic error.

Enthalpies of sublimation were measured using the vacuum sublimation drop microcalorimetric method [11]. Samples (~ 4 mg) of the compound contained in a small, thin glass capillary tube sealed at one end, were dropped at room temperature into the hot reaction vessel in the Calvet high-temperature microcalorimeter, held at 461 K, and then removed from the hot-zone by vacuum sublimation. The observed molar enthalpy of sublimation $[H^0_m(\mathrm{g,461\ K}) - H^0_m(\mathrm{c,298.15\ K})]$ was corrected to 298.15 K using $[H^0_m(\mathrm{g,461\ K}) - \mathrm{H}^0_m(\mathrm{g,298.15\ K})]$ estimated by a group additivity scheme based on data given by Stull et al. [12]. The microcalorimeter was calibrated in situ for these measurements by making use of the reported enthalpy of sublimation of naphthalene [12]. Table 2 lists the experimental results for determining the enthalpy of sublimation of $\mathrm{VO(pd)_2}$, the mean value at 298.15 K is $\Delta_{sub} H^0_m(\mathrm{VO(pd)_2}) = 140.4 \pm 1.1$ kJ mol^{-1}. Measure-

TABLE 2

Enthalpy of sublimation of $VO(pd)_2$

Mass (mg)	T (K)	Δh(obs.) (J)	$\Delta_{sub}H(T)$ (kJ mol^{-1})	$\Delta_{sub}H_m^0$(298.15 K) (kJ mol^{-1})
4.021	461	2.9364	193.63	141.61
4.302	461	3.1447	193.83	141.80
5.089	461	3.6756	191.51	139.49
4.101	461	2.9579	191.25	139.22
4.536	461	3.2828	191.90	139.87

ment of the enthalpies of sublimation of the other complexes was unsuccessful because, for temperatures at which the vapour pressure was sufficiently high to permit vacuum sublimation, partial thermal decomposition occurred.

DISCUSSION

The enthalpies of formation reported in this paper differ from those originally obtained from static-bomb combustion calorimetry. For $V(pd)_3$, the original value was -1649 ± 30 kJ mol^{-1} [2], the reaction calorimetric value is -1522.8 ± 4.5 kJ mol^{-1}, a difference of 126 kJ mol^{-1}; and for $VO(pd)_2$ the corresponding values are in closer agreement, -1372 ± 21 kJ mol^{-1} [1] and -1366.6 ± 7.6 kJ mol^{-1}. Large differences in the results of these two techniques have been noted for other $M(pd)_3$ complexes [3].

To derive the enthalpies of formation of these complexes in the gaseous state, estimates of some enthalpies of sublimation were made. For $V(pd)_3$, the enthalpy of sublimation was estimated to be the same as that for $Cr(pd)_3$, 123 ± 3 kJ mol^{-1} [13]. Comparison of the enthalpies of sublimation of oxine complexes reported by Birkinshaw and Mortimer [14] with corresponding values for pentane-2,4-dionate complexes reported by Ribeiro da Silva [3] suggests that those for oxine complexes are 60 ± 10 kJ mol^{-1} greater than for pentane-2,4-dionate complexes, and the required estimates were made on this basis. Table 3 lists the enthalpies of sublimation and the enthalpies of formation in the crystalline and gaseous states of the complexes studied.

The mean metal–ligand dissociation enthalpy, $\bar{D}$(M–L) in VL_3 may be defined as one third of the enthalpy of the disruption reaction

$$VL_3(g) = V(g) + 3L(g)$$

To obtain $\Delta_f H_m^0$(pd, g), the dissociation enthalpy of the (O–H) bond in the enol form of pentane-2,4-dione is required and various estimates have been proposed ranging from 365 to 430 kJ mol^{-1}. Cavell et al. [15] assessed recent evidence to produce an estimate of 400 ± 20 kJ mol^{-1} and, with the

TABLE 3

Molar values at 298.15 K (kJ mol^{-1})

	$\Delta_f H_m^0(c)$	$\Delta_{sub} H_m^0$	$\Delta_f H_m^0(g)$	$\bar{D}(M-L)$
$V(pd)_3$	-1522.8 ± 4.5	123 ± 3	-1400 ± 5	436 ± 20
$VO(pd)_2$	-1366.6 ± 7.6	140.4 ± 1.1	-1226 ± 8	486 ± 20
$V(ox)_3$	-452.7 ± 4.5	185 ± 10	-268 ± 11	427 ± 12
$VO(ox)_2$	-643.5 ± 7.8	200 ± 10	-444 ± 13	464 ± 12

following $\Delta_f H_m^0$ values (kJ mol^{-1}): Hpd(enol, g), -384.4 ± 1.3 [8]; H(g), 218.00 ± 0.01 [16], then $\Delta_f H_m^0(pd, g) = -202.4 \pm 20.0$ kJ mol^{-1}. To obtain $\Delta_f H_m^0(ox, g)$ it was assumed that the dissociation enthalpy of the (O–H) bond in 8-hydroxyquinoline has the same value as $D(O-H)$ in phenol, 363 ± 9 kJ mol^{-1} [17]. With $\Delta_f H_m^0(Hox, g) = 21.3 \pm 2.1$ kJ mol^{-1} [9], then $\Delta_f H_m^0(ox, g) = 166.3 \pm 10.0$ kJ mol^{-1}. With $\Delta_f H_m^0(V, g) = 514.6 \pm 4.2$ kJ mol^{-1} [7], the mean metal–ligand dissociation enthalpies were derived and are given in Table 3.

The mean metal–ligand dissociation enthalpy, $\bar{D}(M-L)$, in VOL_2 may be defined as one half of the enthalpy of the disruption reaction

$$VOL_2(g) = VO(g) + 2L(g)$$

and with $\Delta_f H_m^0(VO, g) = 151.3 \pm 3.0$ kJ mol^{-1} [7], the $\bar{D}(M-L)$ values given in Table 3 were derived. This derivation assumes that $D(V-O)_{oxo}$ in VOL_2 has the same value as the dissociation enthalpy of the VO molecule and this appears reasonable as the corresponding bond lengths in $VO(pd)_2$ and in VO are the same within experimental error [18].

In general for a series of MX_n molecules, provided there are no large changes in the valence-state excitation energy of M, the mean bond dissociation enthalpy, $\bar{D}(M-X)$, decreases as n increases and normally n increases as the oxidation number of M increases. The data of Table 3 show that $\bar{D}(M-L)$ for L = pd or ox is greater in the V(IV) complex, VOL_2, than in the V(III) complex, VL_3. In the V(IV) complex, VOL_2, five atoms are bonded to vanadium whereas in the V(III) complex, VL_3, the corresponding number is six. This shows that the trends in $\bar{D}(M-X)$ in MX_n molecules are primarily dependent on the number of X ligands and not on the oxidation number of M. Another example is seen in the two molybdenum pentane-2,4-dionates, for it was previously shown that in the Mo(III) complex, $Mo(pd)_3$, and in the Mo(VI) complex, $MoO_2(pd)_2$, $\bar{D}(M-O)_{pd}$ was the same within experimental error [19]. In each complex, six oxygen atoms are bonded to molybdenum although the oxidation states of the two molybdenum atoms are different.

Ribeiro da Silva [3] suggested that the metal–oxygen bonds in metal pentane-2,4-dionates have similarities to the bonds in the corresponding metal oxides as these oxides have polymeric structures in which the metal

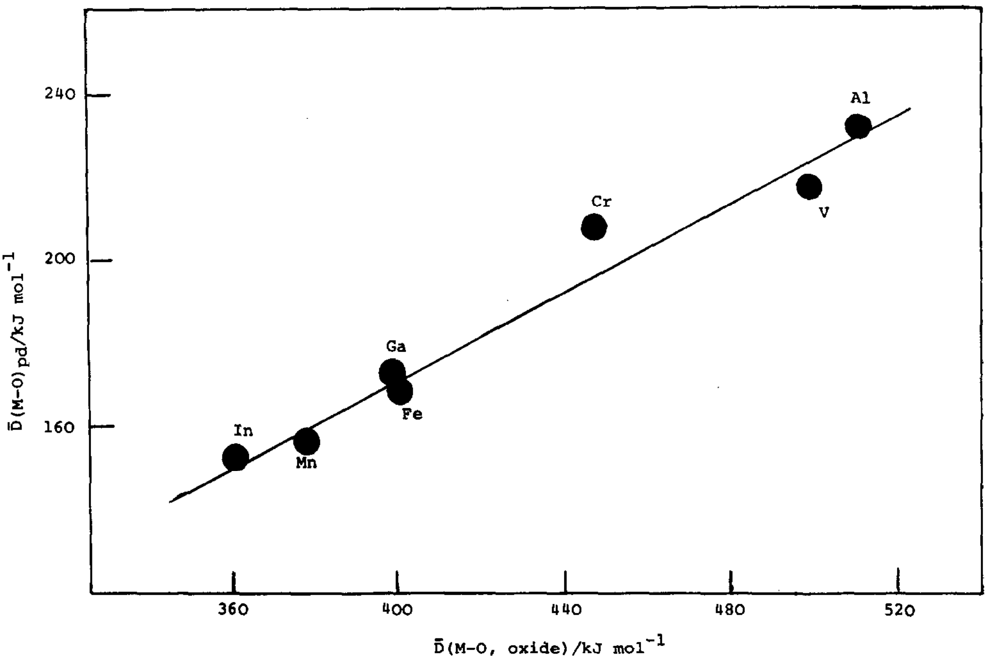

Fig. 1. Variation of $\bar{D}(\mathrm{M{-}O})_{\mathrm{pd}}$ in M(III)(pd)$_3$ with $\bar{D}$(M–O, oxide).

atoms have coordination numbers and configurations similar to those in the metal pentane-2,4-dionates. By considering the dissociation

$$\mathrm{M_2O_3(c) = 2M(g) + 3O(g)}$$

a parameter, $\bar{D}$(M–O, oxide) can be defined as

$$\bar{D}(\mathrm{M{-}O,\ oxide}) = \frac{\Delta H(\mathrm{dissociation})}{\mathrm{Coordination\ no.\ of\ the\ metal}}$$

A plot of $\bar{D}(\mathrm{M{-}O})_{\mathrm{pd}}$ versus $\bar{D}$(M–O, oxide) should be linear. This plot for the M(pd)$_3$ complexes for which this analysis can be made is shown in Fig. 1, where the values for complexes other than V(pd)$_3$ were taken from the review by Ribeiro da Silva [3].

It is apparent that the value reported in this paper for $\bar{D}(\mathrm{V{-}O})_{\mathrm{pd}}$ in V(pd)$_3$, i.e., one half of $\bar{D}$(V–L) in Table 3, fits well with this correlation.

REFERENCES

1 M.M. Jones, B.J. Yow and W.R. May, Inorg. Chem., 1 (1962) 166.
2 J.L. Wood and M.M. Jones, Inorg. Chem., 3 (1964) 1553.
3 M.A.V. Ribeiro da Silva (Ed.), Thermochemistry and its Applications to Chemical and Biological Systems, NATO ASI series, Reidel, Dordrecht, 1984, p. 317.
4 E.H. Jamea and G. Pilcher, Thermochim. Acta, 89 (1985) 1.

5 A.I. Vogel, Quantitative Inorganic Analysis, 4th edn., Longmans, London, 1978.
6 Atomic weights of the elements, Pure Appl. Chem., 51 (1979) 409.
7 V.P. Glysko and V.A. Medvedev, Thermal Constants of Compounds, Akademii Nauk S.S.S.R., Moscow, 1974.
8 J.M. Hacking and G. Pilcher, J. Chem. Thermodyn., 11 (1979) 1015.
9 J.D. Cox and G. Pilcher, Thermochemistry of Organic and Organometallic Compounds, Academic Press, London, 1970.
10 G.L. Bertrand, G.W. Stapleton, C.A. Wulff and L.G. Hepler, Inorg. Chem., 5 (1966) 1283.
11 F.A. Adedeji, D.L.S. Brown, J.A. Connor, M. Leung, M.I. Paz-Andrade and H.A. Skinner, J. Organomet., Chem., 97 (1975) 221.
12 D.R. Stull, E.F. Westrum and G.C. Sinke, The Chemical Thermodynamics of Organic Compounds, Wiley, New York, 1969.
13 H. Naghibi-Bidokhti, Ph.D. Thesis, University of Surrey, U.K., 1977.
14 P.M. Birkinshaw and C.T. Mortimer, J. Chem. Soc., Dalton Trans., (1984) 75.
15 K.J. Cavell, J.A. Connor, G. Pilcher, M.A.V. Ribeiro da Silva, M.D.M.C. Ribeiro da Silva, H.A. Skinner, Y. Virmani and M.T. Zafarani-Moattar, J. Chem. Soc., Faraday Trans. I, 77 (1981) 1585.
16 CODATA, J. Chem. Thermodyn., 10 (1978) 903.
17 D.J. De Frees, R.T. McIver and W.J. Hehre, J. Am. Chem. Soc., 102 (1980) 3334.
18 L.E. Sutton, Interatomic Distances, Chemical Society, London, Spec. Publ. No. 11, 1958, No. 18, 1965.
19 C. Pilcher, K.J. Cavell, C.D. Garner and S. Parkes, J. Chem. Soc., Dalton Trans., (1978) 1311.