Enthalpies of Sublimation of Transition Metal Complexes †

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Enthalpies of sublimation of a number of transition metal complexes have been determined by a differential Knudsen effusion technique in which the effusing vapour has been condensed on a quartz plate, the frequency of oscillation of which depends on the mass of complex deposited.

Mean metal–ligand bond dissociation energies, $\bar{D}$(M–L), in the transition metal complexes ML_nX_2 and ML_n, in which L is a ligand molecule or radical and X is a halogen, can be defined by $\bar{D}(M{-}L) = \Delta H/n$, where ΔH is the enthalpy of the disruption processes (1) and (2).

$$ML_nX_2(g) \longrightarrow MX_2(g) + nL(g) \qquad (1)$$

$$ML_n(g) \longrightarrow M(g) + nL(g) \qquad (2)$$

Values of ΔH can be calculated if the enthalpies of formation of reactants and products are known. Enthalpies of formation of a number of these crystalline complexes are available, but few enthalpies of sublimation have been measured. Lack of this information has hindered calculation of $\bar{D}$(M–L) values. Many transition metal complexes have low vapour pressures at room temperature and tend to decompose on heating to temperatures at which the vapour pressure can be readily measured. Consequently, determination of enthalpy of sublimation, from variation of vapour pressure with temperature, has been possible in only a few favourable cases.

Recently, Yansen *et al.*[1,2] reported the determination of enthalpies of sublimation of a number of nucleic acid bases and related compounds, which have low vapour pressures, by use of the differential Knudsen effusion method in conjunction with a highly sensitive detector. The vapour, which effused from the heated Knudsen cell, was allowed to condense on a quartz crystal positioned above the orifice. By measuring the change in frequency of oscillation of this quartz plate, the rate at which the vapour condensed could be determined with a sensitivity of 10^{-8} g s^{-1}. We have repeated some of their work and also used the technique to determine enthalpies of sublimation of a number of transition metal complexes.

The Clapeyron equation relates the enthalpy of sublimation to the variation of vapour pressure, p, of an ideal gas with temperature as shown in equation (3). According to Knudsen,[3]

$$\Delta H_{sub} = -\boldsymbol{R}\frac{(\mathrm{d}\ln p)}{(\mathrm{d}\ 1/T)} \qquad (3)$$

the rate of mass loss, m', from a cell through a hole of area, a, into an evacuated chamber is related to the vapour pressure by equation (4), in which M is the molar mass of the effusing vapour. In so far as the change in frequency, ν, of the quartz

$$p = \frac{m'}{a}\left(\frac{2\pi RT}{M}\right)^{\frac{1}{2}} \qquad (4)$$

crystal is a measure of the rate of mass loss from the cell, m' may be replaced by ν in equation (4) to give equation (5).

$$\ln p = \ln(\nu T^{\frac{1}{2}}) + \ln\left(\frac{2R}{a^2M}\right)^{\frac{1}{2}} \qquad (5)$$

Consequently, the slope of a plot of $\ln(\nu T^{\frac{1}{2}})$ against $1/T$, when multiplied by $\boldsymbol{R}$, gives a value of ΔH_{sub}.

Experimental

The Edwards 306 vacuum coating unit (which can provide a minimum pressure of 5×10^{-7} Torr), fitted with the FTM3 film thickness monitor incorporating a quartz crystal oscillator (6 MHz), was used with only minor modification. The Knudsen cell was manufactured from a cylindrical piece of brass, external diameter 15 mm, internal diameter 8 mm, open at one end. It was lined with platinum foil. The open end of the cylinder was covered by a piece of platinum foil 0.025 mm thick, pierced with a hole 0.38 mm in diameter. The foil was held in position by a brass screw cap. The cell fitted snugly into the centre of a cylindrical aluminium oven block provided with a proportionally controlled heater circuit. The probe of an Electroplan 2754 platinum resistance thermometer was housed in a tubular cavity drilled into the underside of the aluminium block so that it ran alongside the Knudsen cell. Temperature measurement was made to ±0.1 °C. The quartz oscillator was clamped above the orifice in the Knudsen cell.

With the cell charged with sample (*ca.* 75 mg) the temperature was raised until the rate of sublimation corresponded to a measurable frequency change of *ca.* 10 Hz min^{-1}. When equilibrium was established accurate measurement of the rate of frequency change was made at this and higher temperatures, separated by about 5 K. In three or four subsequent experiments with each compound, different patterns were adopted in which measurements at high temperatures were made before those at lower temperatures, or at alternately higher and lower temperatures, to ensure that the sublimation rates were reproducible.

In a separate experiment, the temperature at which the metal complex began to decompose at atmospheric pressure was established by use of the Perkin-Elmer DSC 1 differential scanning calorimeter. The temperature of the sample in the Knudsen cell was kept well below this decomposition temperature, although for some complexes the temperature range between the threshold of measurable sublimation and the onset of decomposition was small.

On completion of each experiment visual examination of the sample and sublimate was made to confirm that no apparent decomposition had occurred.

The apparatus is not suitable for the study of volatile compounds which sublime readily below a temperature of *ca.* 70 °C, since they fail to condense on the quartz crystal. The crystal could be cooled below 25 °C, but the oscillation frequency is temperature dependent and the sensitivity was diminished. For this reason, the enthalpy of sublimation reported here for salicylaldoxime has been determined by use of the Perkin-Elmer DSC 1 scanning calorimeter according to the technique suggested by Beech and Lintonbon.[4]

Facile decomposition of the following compounds prevented our measuring the rate of sublimation with temperature:

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† *Non-S.I. unit employed:* 1 Torr = (101 325/760) Pa.

[Co(cyt)$_2$Br$_2$] (cyt = cytosine), [Cu(cyt)$_2$Cl$_2$], [Zn(cyt)$_2$Cl$_2$], [Cu(salox)$_2$] [salox = salicylaldoximato, o-C$_6$H$_4$(O$^-$)-CH=NOH], [Cu(alaO)$_2$] (alaO = alaninate), [Pt(glyO)$_2$] (glyO = glycinate), [Co(pd)$_2$] (pd = pentane-2,4-dionate), [Co(pymd)$_2$Cl$_2$] (pymd = pyrimidine-2,4-diol), [Co(thy)$_2$Cl$_2$] (thy = thymine), [Hg(thy)$_2$], *cis*-[Pt(pym)$_2$Cl$_2$] (pym = pyrimidine), and [Pd(mcyt)Cl$_2$] (mcyt = 1-methylcytosine).

Compounds.—Benzanthrone (7*H*-benz[*d,e*]anthracen-7-one; Aldrich Chemical Co., technical grade) was recrystallised twice from xylene, m.p. 170 °C. Cytosine monohydrate (Sigma Chemical Co.) was dried at 130 °C (20 Torr) for 4 h to yield anhydrous cytosine. 1-Methylcytosine was prepared from cytosine by the method of Sakai *et al.*,[5] which yields a compound of empirical formula corresponding to mcyt·SiO$_2$. Passage through an ion-exchange column filled with Amberlite IRA 400 resin, hydroxyl loaded, yielded 1-methylcytosine, m.p. 292 °C (decomp.). Thymine hemihydrate (Sigma Chemical Co.) was dried at 130 °C (20 Torr) for 2 h to yield the anhydrous base.

[M(cyt)$_2$Cl$_2$] (M = Mn or Co) and [M(mcyt)$_2$Cl$_2$] (M = Cd or Hg) were prepared by the methods given in refs. 6 and 7. [M(pd)$_2$] [M = Ni or Cd (Aldrich Chemical Co.); M = Pd or Pt (Johnson Matthey Co.)] were used without further purification; the hygroscopic Cd complex was handled in a dry atmosphere. [Ni(salox)$_2$] was prepared by literature methods.[8,9] [M(glyO)$_2$] (M = Ni or Cu) were prepared [10,11] and dried *in vacuo* at 100 °C (20 Torr) for 6 h. [M(Hdmg)$_2$] [Hdmg = dimethylglyoximate(1−); M = Ni or Pt] were prepared by literature methods; [8,12] both species precipitate from aqueous solution as anhydrates. [M(hoqu)$_2$] (hoqu = 8-hydroxyquinolinate; M = Mn, Co, Ni, Cu, Zn, Cd, or Pd) were prepared according to the methods given in refs. 8 and 13, with prolonged drying *in vacuo* at 120 (M = Cu), 140 (M = Mn, Ni, Pd, and Zn), 160 (M = Cd), and 220 °C (M = Co), as recommended by Duval.[14] The copper complex was the α form. Satisfactory microanalyses were obtained for all compounds except for the platinum dimethylgloximate complex which yielded unreproducible results even with the addition of WO$_3$ to the sample.

Mass Spectrometry.—In order to define the nature of the vapour phase species present during the sublimation experiments, mass spectra of the substrates were examined over the same temperature ranges used in these experiments.

The A.E.I. MS 12 spectrometer with direct injection port was used. The operating conditions were as follows: slit width 4 mm; electron impact source, ionization potential 70 eV; electron multiplier voltage 2.5 kV; scans were carried out over a range 0—900 m/e. Appearance potentials were recorded at 2.5 or 1.7 kV. A reduced ionization potential of 10.5 eV was employed for selected measurements.

For the metal complexes only gaseous monomers were detected. Whilst those findings do not entirely exclude gas-phase association in the Knudsen effusion experiments, we make the assumption that the enthalpies of sublimation refer to monomeric species. For cytosine and 1-methylcytosine, mass spectra indicated that a mixture of monomer and dimer is generated over the temperature ranges used in the Knudsen effusion experiments. For cytosine, using a reduced ionization potential of 10.5 eV, comparison of apparent dimer–monomer ion intensities, I^+, suggests the following ratios: 160 °C, 50 : 50; 210 °C, 5 : 95; 240 °C, 0.5 : 99.5 (dimer : monomer). Above 260 °C there was no evidence of dimer formation. An approximate value for the enthalpy, $\Delta H^{473} = 5.7 \pm 1.2$ kJ mol^{-1}, of the reaction cytosine (dimer) $\longrightarrow$ 2 cytosine (monomer) can be calculated from a plot of ln K against $1/T$, if the ion intensities of dimer and monomer at each temperature are taken to reflect equilibrium concentrations. A plot of ln (I^+T) against $1/T$ for the monomer gives an apparent value of $\Delta H_{\text{sub}}^{495} = 135$ kJ mol^{-1}, which is in good agreement with the value obtained from Knudsen effusion. Mass spectra of 1-methylcytosine were less reproducible, but indicated traces of dimer at 170 °C and only monomer at 260 °C. Yansen *et al.*[2] have also reported that 1-methylcytosine is difficult to study by electron impact techniques.

Results and Discussion

The Table shows values of enthalpies of sublimation, $\Delta H_{\text{sub}}^{T}$, which refer to the mean temperature, T, of the range over which measurements were made. The error limits are mean uncertainty intervals, *i.e.* twice the standard deviations of mean values. In the absence of values for ΔC_p, the difference between the specific heats of the compounds in the solid and gas phases, it is not possible to calculate accurately the correction to be applied to $\Delta H_{\text{sub}}^{T}$ to yield the values $\Delta H_{\text{sub}}^{298}$. Various attempts have been made to estimate the magnitude of this correction. Sabbah *et al.*[15] have measured values of $\Delta H_{\text{sub}}^{T}$ for aminobenzoic acids at various temperatures, T, and have extrapolated the linear plot of $\Delta H_{\text{sub}}^{T}$ against T to give a value $\Delta H_{\text{sub}}^{298}$. The relationship, $\Delta H_{\text{sub}}^{298} = \Delta H_{\text{sub}}^{T} + (298.15 - T)\Delta C_p$, yields a value of ΔC_p in the region −50 to −60 J K^{-1} mol^{-1}. For bis(pentane-2,4-dionato) complexes Melia and Merrifield [16] have used the estimated value $\Delta C_p = -40$ J K^{-1} mol^{-1}. Whilst de Kruif *et al.*[17d] have considered a value of $-(60 \pm 20)$ J K^{-1} mol^{-1} to be reasonable for a series of amino acids and peptides. Pedley [18] has suggested that the statistical thermodynamic difference is 6$\boldsymbol{R}$ or $\Delta C_p = -50$ J K^{-1} mol^{-1}. We adopt this figure in our calculations.

For benzanthrone there are two previously reported values for the enthalpy of sublimation, $\Delta H_{\text{sub}}^{398} = 115.5$ kJ mol^{-1}, found by Inokuchi *et al.*[19] and also the value 114.2 ± 0.8 kJ mol^{-1} given by Yansen *et al.*,[2] although the temperature to which it refers is not quoted. Our value is $\Delta H_{\text{sub}}^{370} = 119.7 \pm 5.4$ kJ mol^{-1}. It should be noted that this compound polymerises at higher temperatures *in vacuo* and care must be taken that too high a temperature is not used for the sublimation experiment. Our value for cytosine, $\Delta H_{\text{sub}}^{453} = 148.9 \pm 2.6$ kJ mol^{-1} of monomer, which includes a correction of 1.7 kJ mol^{-1} for the dissociation of a fraction of dimer to monomer, may be compared with the value $\Delta H_{\text{sub}}^{458} = 150.6 \pm 1.5$ kJ mol^{-1}, obtained by Yansen *et al.*[1,2] using the same technique, and with Sabbah's [20] value of $\Delta H_{\text{sub}}^{458} = 149.0 \pm 2.5$ kJ mol^{-1}. Sabbah [20] has also measured the enthalpy of sublimation at temperatures between 448 and 468 K and has extrapolated a linear plot of the somewhat scattered points to yield $\Delta H_{\text{sub}}^{298} = 176 \pm 10$ kJ mol^{-1}.

For 1-methylcytosine, our value of $\Delta H_{\text{sub}}^{433} = 141.8 \pm 8.8$ kJ mol^{-1} is close to that found by Yansen *et al.*[2] (142.7 ± 2.0 kJ mol^{-1}) from field ionization mass spectrometry, although the temperature to which the latter value refers is not given.

Our value of $\Delta H_{\text{sub}}^{410} = 125.7 \pm 3.6$ kJ mol^{-1} for thymine is close to that of Yansen *et al.*[2] ($\Delta H_{\text{sub}}^{408} = 124.3 \pm 1.2$ kJ mol^{-1}) and to $\Delta H_{\text{sub}}^{434} = 121.0 \pm 1.8$ kJ mol^{-1} found by Nabavian *et al.*,[21] who also quote $\Delta H_{\text{sub}}^{298} = 134.1 \pm 4.2$ kJ mol^{-1}, obtained by extrapolation.

When values for the enthalpies of sublimation of transition metal complexes have not been available, a number of authors have assumed these values to be the same as those of the uncomplexed ligand. The values in the Table show this to be the case, to within ±10 kJ mol^{-1}, for only [Co(cyt)$_2$Cl$_2$], [Mn(cyt)$_2$Cl$_2$], [Ni(glyO)$_2$], and possibly [Ni(salox)$_2$]. Only where the structure of the crystalline ligand remains virtually unchanged on complexing with the metal, so that inter-

Table. Enthalpies of sublimation

Compound	$\Delta H_{sub}{}^{T}$/ kJ mol^{-1}	Temp. range (K)	$\Delta H_{sub}{}^{298}$/ kJ mol^{-1}
Benzanthrone	119.7 ± 5.4	353—388	124.6 ± 6
Cytosine	147.2 ± 2.6	423—483	155.0 ± 3
1-Methylcytosine	141.8 ± 8.8	423—443	149.1 ± 9
Thymine	125.7 ± 3.6	383—438	131.3 ± 4
Salicylaldoxime	96.7 ± 9.4 [a]	423—513	105.2 ± 10
8-Hydroxyquinoline			108.8 ± 10 [b]
Glycine			140.0 ± 5 [c]
Pentane-2,4-dione			68.0 ± 10 [d]
Dimethylglyoxime			97.1 ± 1 [e]
$[Co(cyt)_2Cl_2]$	151.8 ± 14	483—523	162 ± 14
$[Mn(cyt)_2Cl_2]$	146.0 ± 21 [f]	433—453	153 ± 21
$[Cd(mcyt)_2Cl_2]$	135.3 ± 20	483—503	145 ± 20
$[Hg(mcyt)_2Cl_2]$	150.8 ± 19	428—443	159 ± 19
$[Ni(pd)_2]$	127.7 ± 10	378—403	132 ± 10
$[Pd(pd)_2]$	127.6 ± 17	363—393	132 ± 17
$[Pt(pd)_2]$	129.4 ± 9	363—383	133 ± 9
$[Cd(pd)_2]$	144.9 ± 22	438—448	154 ± 22
$[Ni(salox)_2]$	106.6 ± 29	403—423	112 ± 29
$[Ni(glyO)_2]$	119.7 ± 9	388—423	125 ± 10
$[Cu(glyO)_2]$	102.5 ± 15	443—493	111 ± 15
$[Ni(Hdmg)_2]$	131.1 ± 6	433—473	139 ± 6
$[Pt(Hdmg)_2]$	145.8 ± 13	423—468	153 ± 13
$[Mn(hoqu)_2]$	208.4 ± 14	615—650	226 ± 14
$[Co(hoqu)_2]$	185.7 ± 9	533—569	200 ± 10
$[Ni(hoqu)_2]$	129.9 ± 6	468—503	139 ± 6
$[Cu(hoqu)_2]$	160.3 ± 3	478—503	170 ± 3
$[Zn(hoqu)_2]$	167.9 ± 6	473—513	178 ± 6
$[Cd(hoqu)_2]$	144.9 ± 22	438—448	154 ± 22
$[Pd(hoqu)_2]$	158.5 ± 4	483—503	168 ± 4

[a] From differential scanning calorimetry. [b] G. R. Horton and W. W. Wendlandt, *J. Inorg. Nucl. Chem.*, 1963, **25**, 241. [c] Weighted mean of values in ref. 17, corrected to 298 K. [d] ΔH_{vap} from J. B. Pedley and J. Rylance (CATCH Data, Organic and Organometallic Compounds, University of Sussex, 1977), assuming $\Delta H_{fusion} = 24$ kJ mol^{-1}. [e] From Pedley and Rylance (footnote *d*). [f] Value uncertain, evidence of decomposition.

molecular forces will be similar in both the uncomplexed ligand and metal complex, do we expect the enthalpies of sublimation to be similar. Unfortunately, there are insufficient structural data to take this analysis further. Of the complexes studied, structural information is available for only the following anhydrous compounds: $[Ni(pd)_2]$,[22] $[Pd(pd)_2]$,[23] $[Pt(pd)_2]$,[24] $[Ni(salox)_2]$,[25] $[Ni(Hdmg)_2]$,[26] $[Pt(Hdmg)_2]$,[27] α-$[Cu(hoqu)_2]$,[28] and $[Pd(hoqu)_2]$.[29] Except for $[Ni(salox)_2]$, the intermolecular hydrogen bonding in the parent ligand[30-32] differs considerably from that in the complex. The structure of crystalline pentane-2,4-dione has not been determined, but that of 1-phenylbutane-1,3-dione is known.[33] In salicylaldoxime, there appears to be little long-range ordering and this situation persists in the nickel complex.

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