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THE THERMOCHEMISTRY OF CARBONYL COMPLEXES OF Cr, Mo AND W WITH PYRIDINE AND ACETONITRILE *

FESTUS A. ADEDEJI, JOSEPH A. CONNOR, CHRISTOPHER P. DEMAIN, JOSE A. MARTINHO-SIMOES, HENRY A. SKINNER and MOHAMED T. ZAFARANI MOATTAR
Department of Chemistry, University of Manchester, Manchester, M13 9PL (Great Britain)

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Summary

Microcalorimetric measurements at elevated temperatures of the heats of thermal decomposition and of iodination of a number of $[M(CO)_nL_{6-n}]$ complexes (M = Cr, Mo, W; $n = 3, 4$; L = py, MeCN) have led to values for the standard enthalpies of formation of the following crystalline compounds (values given in kJ mol^{-1}) at 25°C: *fac*-$[Mo(CO)_3py_3]$ —(275 ± 12), *fac*-$[Mo(CO)_3(NCCH_3)_3]$ —(410 ± 12), *fac*-$[W(CO)_3py_3]$ —(250 ± 12), *fac*-$[W(CO)_3(NCCH_3)_3]$ —(405 ± 12) and *cis*-$[Cr(CO)_4py_2]$ —(505 ± 20). From these and other data, including estimated heats of sublimation, the bond enthalpy contributions of the various metal—ligand bonds in the gaseous metal complexes were evaluated as follows (values in kJ mol^{-1}): D(Cr—py) 102, D(Mo—py) 146, D(W—Py) 173, D(Mo—NCMe) 135 and D(W—NCMe) 169. For a given metal the bond enthalpy contribution decreased in the order $D(M{-}CO) > D(M{-}py) > D(M{-}NCMe)$. This order is related to the σ- and π-bonding character of the ligand.

Introduction

The enthalpies of formation of several crystalline complexes of the type $[ML_nX_2]$ (where M is a transition metal; L is pyridine, or a substituted pyridine; $n = 2$ or 4; and X = Cl, Br or I) have been measured, and are tabulated and discussed elsewhere by Ashcroft and Mortimer [1]. The data provide values for the enthalpies of thermal decomposition of the solid complexes, but only in a few cases are heats of sublimation of the complexes known, which are necessary to evaluate the heats of decomposition in the gaseous state, ΔH_1 (eq. 1).

$$[ML_nX_2](g) \rightarrow nL(g) + MX_2(g);\ \Delta H_1 \qquad (1)$$

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* No reprints available.

ΔH_1 values are available [2] for the complexes [CoL_2X_2], (L = pyridine, 2-methylpyridine, 2- and 3-chloropyridine, 2- and 3-bromopyridine; X = Cl and Br), [NiL_2Cl_2] (L = 3-chloro and 3-bromopyridine), and [CuL_2Cl_2] (L = 3-bromopyridine). The quantities $\Delta H_1/2$ give the mean bond dissociation enthalpies, $\bar{D}$(L—M), of the metal—ligand bonds; for the complexes of cobalt $\bar{D}$ values ranged from 122—160 kJ mol^{-1}, the average (10 compounds), $\bar{D} \sim 134$ kJ mol^{-1}, comparing closely with the mean bond dissociation enthalpy in cobalt carbonyls [3] $\bar{D}$(Co—CO) 134 kJ mol^{-1}. Similarly, in the nickel complexes, the mean $\bar{D}$(L—Ni) of approximately 160 kJ mol^{-1} compares in magnitude with $\bar{D}$(Ni—CO) in nickel carbonyl [3] (147 kJ mol^{-1}).

Measurements of the enthalpies of displacement of pyridine by carbon monoxide in the complex [$W(CO)_5py$], and of displacement of acetonitrile by carbon monoxide in the complexes [$W(CO)_5(CH_3CN)$], *cis*-[$W(CO)_4(CH_3CN)_2$] and *fac*-[$W(CO)_3(CH_3CN)_3$] have been reported recently by Vrieze and co-workers [4,5]. Although the interpretation of the results obtained depends on heats of sublimation of uncertain reliability, the indications are that $\bar{D}$(py—W) and $\bar{D}$(CH_3CN—W) are of comparable magnitude to $\bar{D}$(W—CO).

The present studies have involved measurements of the enthalpies of thermal decomposition of *fac*-[$Mo(CO)_3py_3$], *fac*-[$W(CO)_3py_3$], *cis*-[$Cr(CO)_4py_2$] and of *fac*-[$Mo(CO)_3(NCMe)_3$] and *fac*-[$W(CO)_3(NCMe)_3$] by microcalorimetric methods. In complementary studies, measurements have been made of the enthalpies of direct synthesis of *fac*-[$Mo(CO)_3py_3$] and *fac*-[$W(CO)_3py_3$].

Experimental

Calorimeter

The Calvet high temperature twin-cell microcalorimeter was used, as described in previous papers [6,7].

Compounds

Samples of *fac*-[$M(CO)_3py_3$] (M = Mo, W) and of *cis*-[$Cr(CO)_4py_2$] were prepared by refluxing the carbonyls with pyridine, and precipitation of the product. Samples of *fac*-[$M(CO)_3(NCMe)_3$] (M = Mo, W) were prepared as described by Tate, Knipple and Augl [8]. The purity of the complexes was established by microanalysis, and by spectroscopic measurements.

Auxiliary data

All heat quantities are given in joules (J) or in kilojoules (kJ). The following auxiliary heat of formation data (kJ mol^{-1}) were used in evaluating the experimental results: $\Delta H_f^\circ(CO,g) = -(110.524 \pm 0.17)$ [9]; $\Delta H_f^\circ(\text{pyridine},g) = (144.56 \pm 0.5)$ [11]; $\Delta H_f^\circ(I_2,g) = (62.442 \pm 0.04)$ [10]; $\Delta H_f^\circ(\text{acetonitrile},g) = (73.72 \pm 0.80)$ [12]; $\Delta H_f^\circ(Cr,g) = (396.6 \pm 4)$ [9]; $\Delta H_f^\circ(Cr(CO)_6,g) = -(908.3 \pm 1.7)$ [13]; $\Delta H_f^\circ(Mo,g) = (658.1 \pm 4)$ [9]; $\Delta H_f^\circ(Mo(CO)_6,g) = -(915.9 \pm 1.7)$ [13]; $\Delta H_f^\circ(W,g) = (851.0 \pm 6)$ [10]; $\Delta H_f^\circ(W(CO)_6,g) = -(883.7 \pm 3.3)$ [13]; $\Delta H_f^\circ(CrI_2,c) = -(156.9 \pm 4)$ [9]; $\Delta H_f^\circ(MoI_3,c) = -(113.0 \pm 10.5)$ [14]; $\Delta H_f^\circ(CrI_3,c) = -(205.0 \pm 4)$ [9]; $\Delta H_f^\circ(WI_3,c) = -(46.0 \pm 12.5)$ [14]; $\Delta H_f^\circ(Cr(CO)_6,c) = -(979.9 \pm 2)$ [13]; $\Delta H_f^\circ(W(CO)_6,c) = -(960.2 \pm 3)$ [13]; $\Delta H_f^\circ(Mo(CO)_6,c) = -(989.5 \pm 1)$ [13]; $\Delta H_f^\circ(\text{pyridine},l) = (104.35 \pm 0.5)$ [11].

To reduce ΔH^{T} values to ΔH^{298}, $(H^{T} - H^{298})$ data for the metals were taken from the compilation of Hultgren, Orr, Anderson and Kelley [15], and data for pyridine and acetonitrile vapours from the compilation of Stull, Westrum and Sinke [16].

Results

1. Trispyridinemolybdenum tricarbonyl, [Mo(CO)$_3$(C$_5$H$_5$N)$_3$]

The vacuum sublimation microcalorimetric technique was applied at temperatures from 395—481 K. Thermal decomposition was induced on evacuation, molybdenum metal depositing as a black powder in the capillary tube containers. Decomposition was slow at 395 K, and at 423 K appreciable amounts of $Mo(CO)_6$ escaped the hot-zone undecomposed. At temperatures >450 K the decomposition was more nearly complete, and the amounts of $Mo(CO)_6$ escaping undecomposed were usually small (<5%). Typical results are summarized in Table 1. The measured $\Delta H^{\star}_{\text{dec.}}$ provide only a lower limit for the total decomposition (eq. 2), no allowance having been made for partial decomposition

$$[Mo(CO)_3py_3]\,(c,\,298) \rightarrow 3py(g,T) + 3CO(g,T) + Mo(c,T) \qquad (2)$$

(eq. 2a), nor for exothermal effects due to absorption of CO and of pyridine

$$[Mo(CO)_3py_3]\,(c,\,298) \rightarrow 3py(g,T) + 1/2Mo(CO)_6(g,T) + 1/2Mo(c,T) \qquad (2a)$$

vapour on the metal powder deposit. At the higher temperatures ($T > 450$ K), the partial decomposition (eq. 2a) was only of marginal importance, but the effects of chemisorption were seemingly responsible for a considerable lowering of $\Delta H^{\star}_{\text{dec.}}$. (The highest measured $\Delta H^{\star}_{\text{dec.}} \sim 394$ kJ mol^{-1} at 450 K corresponds to $\Delta H^{\circ}_{f}[Mo(CO)_3py_3](c) \sim -229$ kJ mol^{-1}, which, from other measurements, appears to be too high by ca. 50 kJ mol^{-1}). At the lower range of temperatures, there was noticeable escape of $Mo(CO)_6$ from the hot-zone, and the partial decomposition mode (eq. 2a) may become the dominant one below 420 K. If we attribute the measured $\Delta H^{\star}_{\text{dec.}}$ 315 kJ mol^{-1} at 423 K exclusively to reaction 2a, the derived ΔH°_{f} for $[Mo(CO)_3py_3](c)$ is -289 kJ mol^{-1}; this latter we consider as a lower limit, $\Delta H^{\circ}_{f} \geqslant -289$ kJ mol^{-1}.

The drop microcalorimetric technique was applied to measure the heat of reaction of molybdenum hexacarbonyl with excess pyridine vapour at temperatures in the range 417—422 K. Figure 1 shows a typical thermogram: the initial endotherm records the vaporization of the pyridine sample, and the second

TABLE 1

THERMAL DECOMPOSITION OF $[Mo(CO)_3py_3]$

T (K)	$Mo(CO)_3py_3$ (mg)	$\Delta H^{\star}_{\text{dec.}}$ (kJ mol^{-1})	$\Delta H^{298}_{\text{dec.}}$ (kJ mol^{-1})
423	4.835	315	265
431	5.265	375	321
450	4.105	390	327
450	3.415	394	331
451	6.175	392	329

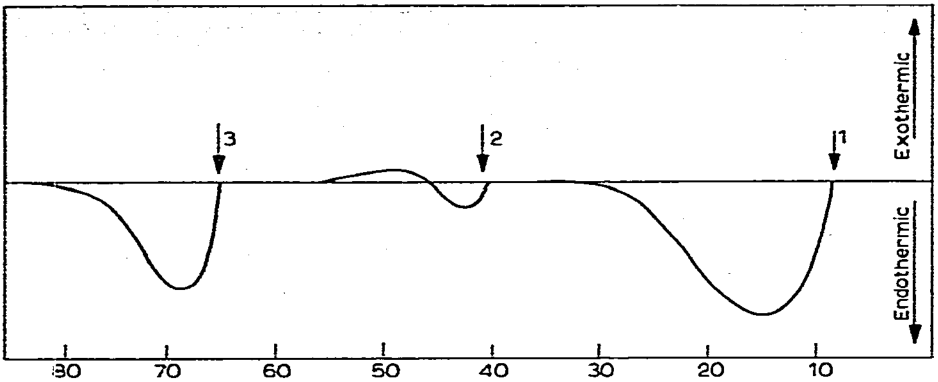

Fig. 1. Thermogram for pyridine-$Mo(CO)_6$ reaction. 1. Pyridine sample introduced; 2. $Mo(CO)_6$ sample introduced; 3. Reaction vessel evacuated.

records the sublimation and reaction of the $Mo(CO)_6$ sample, introduced later. The reaction was allowed to continue for a period of 20—30 minutes, after which the reaction vessel was evacuated, thereby inducing thermal decomposition of the products formed, recorded in the third endotherm of Fig. 1.

The amount of *fac*-$[Mo(CO)_3py_3]$ formed was determined by dissolving the Mo deposit in nitric acid, and analysis of the solution for total Mo content. An indirect estimate was also obtained from the area of the decomposition endotherm. The thermal results are summarized in Table 2. The measured heats of the cell reaction, $\Delta h^{\star}_{\text{obs.}}$, arise from complex formation, $\Delta h^{\star}_{r}$, and from vaporization of unreacted $Mo(CO)_6$, $\Delta h^{\star}_{\text{vap.}}$, ($\Delta h^{\star}_{\text{obs.}} = \Delta h^{\star}_{r} + \Delta h^{\star}_{\text{vap.}}$). The column headed x% gives the percentage of $Mo(CO)_6$ escaping reaction. Although the products of reaction probably contained both $[Mo(CO)_5py]$ and *cis*-$[Mo(CO)_4py_2]$ admixed with *fac*-$[Mo(CO)_3py_3]$, the results are evaluated initially on the assumption that the product was exclusively the tripyridine complex. $\Delta H^{\star}_{r}$ then relates to reaction 3. ΔH^{298}_{r} refers to this same reaction carried out isothermally at 298 K.

$$Mo(CO)_6(c,298) + 3C_5H_5N(g,T) \rightarrow [Mo(CO)_3(C_5H_5N)_3](c,T) + 3CO(g,T) \qquad (3)$$

The mean value of $\Delta H^{298}_{r} = -(50.4 \pm 7)$ kJ mol^{-1} corresponds to $\Delta H^{\circ}_{f}[Mo(CO)_3py_3,c] = -(274.6 \pm 8)$ kJ mol^{-1} (Table 2).

TABLE 2

REACTION OF $Mo(CO)_6$ WITH PYRIDINE

T (K)	$Mo(CO)_6$ (mg)	C_5H_5N (mg)	$\Delta h^{\star}_{\text{obs.}}$ (J)	x (%)	$\Delta h^{\star}_{\text{vap.}}$ (J)	$\Delta h^{\star}_{r}$ (J)	$\Delta H^{\star}_{r}$ (kJ mol^{-1})	ΔH^{298}_{r} (kJ mol^{-1})
417	2.205	3.405	0.068	29	0.242	—0.174	—29.4	—48.7
420	2.115	3.570	0.106	29	0.234	—0.128	—22.5	—42.1
417	2.370	3.510	0.199	40	0.360	—0.161	—26.8	—46.1
422	2.365	4.520	0.018	31	0.282	—0.264	—42.7	—62.5
413	2.020	3.270	0.087	34	0.258	—0.171	—33.9	—52.8

TABLE 3

THERMAL DECOMPOSITION OF [$W(CO)_3py_3$]

T (K)	$W(CO)_3py_3$ (mg)	Method	$\Delta H^{\star}_{dec.}$ (kJ mol^{-1})	$\Delta H^{298}_{dec.}$ (kJ mol^{-1})
423	4.350	VS/TD	366	316
451	4.010	VS/TD	396	333
451	3.670	VS/TD	392	328
451	3.550	VS/TD	385	321
489	5.450	TD	374	293
513	3.750	TD	383	291
510	3.680	TD	383	292

2. *Trispyridinetungsten tricarbonyl, [$W(CO)_3(C_5H_5N)_3$]*

The vacuum sublimation technique was applied at temperatures over the range 422—474 K, and resulted in thermal decomposition with deposition of tungsten metal as a black powder within the capillary tube containers at all temperatures. Small amounts of $W(CO)_6$ escaped the hot zone without decomposition to condense in the cold trap of the exit vacuum line. Results of these, and of thermal decomposition measurements at higher temperatures, are included in Table 3.

The mean $\Delta H^{298}_{dec.}$ from vacuum sublimation/thermal decomposition (VS/TD) studies (324.5 kJ mol^{-1}) is appreciably higher than from thermal decomposition measurements (292 kJ mol^{-1}) at high temperatures (489—513 K), but both values are low due to incomplete decomposition ($W(CO)_6$ escaping from the hot zone) and to surface absorption on the metal deposit. The higher value corresponds to $\Delta H^{\circ}_f([W(CO)_3py_3],(c)) = -222.4$ kJ mol^{-1}.

Measurements of the heat of reaction of tungsten hexacarbonyl with excess pyridine vapour were made at temperatures in the range 422—439 K in similar manner to those made with $Mo(CO)_6$ and pyridine. On evacuation at the end of the reaction, a white deposit of unreacted $W(CO)_6$ condensed in the cooler part of the exit line, and below this a small deposit (0.1—0.3 mg) pale yellow in colour, less volatile than the hexacarbonyl, which is thought to be [$W(CO)_5py$]. The thermal results are summarized in Table 4, and were evaluated as already described for the similar reaction of $Mo(CO)_6$ and pyridine.

The mean value of $\Delta H_r^{298} = -(54.7 \pm 8.4)$ kJ mol^{-1} corresponds to ΔH°_f-[$W(CO)_3py_3$, c] $= -(249.7 \pm 9)$ kJ mol^{-1} (Table 3).

TABLE 4

REACTION OF $W(CO)_6$ WITH PYRIDINE

T (K)	$W(CO)_6$ (mg)	C_5H_5N (mg)	$\Delta h^{\star}_{obs.}$ (J)	x (%)	$\Delta h^{\star}_{vap.}$ (J)	$\Delta h^{\star}_r$ (J)	$\Delta H^{\star}_r$ (kJ mol^{-1})	ΔH^{298}_r (kJ mol^{-1})
422	1.910	3.140	0.206	55	0.308	−0.120	−41.4	−63.1
422	1.875	3.450	0.209	52	0.286	−0.077	−29.8	−51.5
430	3.010	3.490	0.358	56	0.508	−0.150	−40.1	−62.4
431	3.080	3.300	0.410	53	0.490	−0.080	−19.3	−41.7
439	3.200	3.445	0.386	53	0.519	−0.133	−31.0	−54.3

3. *Dipyridinechromium tetracarbonyl, [Cr(CO)$_4$py$_2$]*

Vacuum sublimation studies over the range 392—456 K led to thermal decomposition, the chromium depositing as a black powder within the capillary tube containers. Some $Cr(CO)_6$ escaped the hot-zone without decomposition, to condense with pyridine in the cold trap in the exit vacuum line. Thermal decomposition appeared to be complete on dropping samples into the argon-filled reaction vessel at temperatures in the range 512—519 K. Typical results are summarized in Table 5.

The $\Delta H^{*}_{dec.}$ values from thermal decomposition at the higher range of temperature are lowered due to exothermal surface absorption of CO and pyridine on the chromium deposit. At the lower range of temperatures, the $\Delta H^{*}_{dec.}$ values are probably less affected by surface effects, but now refer to incomplete decomposition. The limit of this would ascribe the observed $\Delta H^{*}_{dec.}$ to the partial decomposition shown in eq. 4. Insofar as decomposition over the range 392—

$$[Cr(CO)_4py_2](c,298) \rightarrow 2py(g,T) + 1/3\ Cr(c,T) + 2/3\ Cr(CO)_6(g,T) \qquad (4)$$

409 K approximates to eq. 4, the mean $\Delta H^{298}_{dec} \sim 199$ kJ mol^{-1} then gives $\Delta H^{\circ}_{f}[Cr(CO)_4py_2, c] \sim -515$ kJ mol^{-1}, which we consider as a lower limit.

4. *Tris(acetonitrile)molybdenum tricarbonyl, [Mo(CO)$_3$(NCCH$_3$)$_3$]*

Thermal decomposition in argon appeared to be complete at 507 K, but the measured heats of decomposition ($\Delta H^{507}_{dec.} \sim 297$ kJ mol^{-1}) are lowered by surface adsorption and reaction of CO and CH_3CN on the active metallic deposit. Similar studies at 456 K gave a thin grey metallic mirror on the walls of the reaction vessel, and a black metal powder remained in the capillary tube containers; decomposition was incomplete, appreciable amounts of $Mo(CO)_6$ escaping the hot-zone to condense in cool parts of the exit line. The measured heat of decomposition, $\Delta H^{456}_{dec.} \sim 218$ kJ mol^{-1} related to partial decomposition as shown in eq. 5 where $x \geqslant 0.5$ and < 1. The value of x was not determined

$$[Mo(CO)_3(NCCH_3)_3](c,298) \rightarrow$$

$$3CH_3CN(g,456) + xMo(c,456) + 3(2x - 1)CO(g,456) + (1 - x)(Mo(CO)_6(g,456) \qquad (5)$$

analytically, but to judge visually by the amount of $Mo(CO)_6$ escaping decompo-

TABLE 5

THERMAL DECOMPOSITION OF [Cr(CO)$_4$py$_2$]

T (K)	$Cr(CO)_4py_2$ (mg)	Method	$\Delta H^{*}_{dec.}$ (kJ mol^{-1})	$\Delta H^{298}_{dec.}$ (kJ mol^{-1})
392	3.165	VS/TD	226	195
403	4.160	VS/TD	238	204
409	4.090	VS/TD	233	199
456	3.835	VS/TD	245	191
512	2.460	TD	310	234
519	2.150	TD	299	219

TABLE 6

IODINATION OF $[Mo(CO)_3(NCCH_3)_3]$

T (K)	$Mo(CO)_3(NCCH_3)_3$ (mg)	I_2 (mg)	n	$\Delta H^{\star}_{iod.}$ (kJ mol^{-1})	$\Delta H^{\star}_{dec.}$ (kJ mol^{-1})	$\Delta H^{298}_{dec.}$ (kJ mol^{-1})
459	4.350	11.385	2.67	173	359	312
460	3.555	10.700	2.47	180	352	304
460	3.625	10.515	2.60	156	337	290
461	3.380	11.670	2.76	153	345	297
			Mean $\Delta H^{298}_{dec.}$ = 301 kJ mol^{-1}			

sition, x appeared to lie nearer to the limit $x = 0.5$ than to $x = 1$. The limiting value $x = 0.5$, combined with $\Delta H^{298}_{dec.}$ ~172 kJ mol^{-1} (on correcting $\Delta H^{456}_{dec.}$ to 298 K), leads to $\Delta H^{\circ}_{f}[Mo(CO)_3(NCCH_3)_3,c] = -409$ kJ mol^{-1}.

More satisfactory results were obtained from measurements of the heat of reaction of $[Mo(CO)_3(NCCH_3)_3]$ with iodine vapour at temperatures in the range 459—461 K. Results are summarized in Table 6.

$\Delta H^{\star}_{iod.}$ refers to the calorimeter reaction 6 and $\Delta H^{\star}_{dec.}$ to the thermal decomposition (eq. 7) obtained on correcting $\Delta H^{\star}_{iod.}$ for the exothermic heat of formation of MoI_n from Mo(c) and I_2(g). The mean value, $\Delta H^{298}_{dec.} = (301 \pm 9)$ kJ mol^{-1} corresponds to $\Delta H^{\circ}_{f}[Mo(CO)_3(NCCH_3)_3, c] = -(410 \pm 10)$ kJ mol^{-1}.

$$[Mo(CO)_3(NCCH_3)_3](c,298) + \frac{n}{2} I_2(g,T) \rightarrow MoI_n(c,T) + 3CO(g,T) + 3CH_3CN(g,T) \qquad (6)$$

$$[Mo(CO)_3(NCCH_3)_3](c,298) \rightarrow Mo(c,T) + 3CO(g,T) + 3CH_3CN(g,T) \qquad (7)$$

5. *Tris(acetonitrile)tungsten tricarbonyl, $[W(CO)_3(NCCH_3)_3]$*

Measurements by the vacuum sublimation technique over the range 389—460 K led to thermal decomposition of the sample, the metal remaining as a black powder in the capillary tube container. There was no mirror formation on the walls of the reaction vessel, and $W(CO)_6$ vapour escaped without decomposition from the hot zone to be trapped out on a cold finger in the exit vacuum line. The measured heats of decomposition ($\Delta H^{\star}_{dec.}$, Table 7) are presumed to relate to the partial decomposition, shown in eq. 8, where $x \geqslant 0.5$ and < 1. Analyses

TABLE 7

THERMAL DECOMPOSITION OF $[W(CO)_3(NCCH_3)_3]$

T (K)	$W(CO)_3(NCCH_3)_3$ (mg)	Method	$\Delta H^{\star}_{dec.}$ (kJ mol^{-1})
389	3.695	VS/TD	226
393	5.600	VS/TD	222
394	4.740	VS/TD	223
420	5.010	VS/TD	215
459	3.035	VS/TD	200

TABLE 8

IODINATION OF $[W(CO)_3(NCCH_3)_3]$

T (K)	$W(CO)_3(NCCH_3)_3$ (mg)	I_2 (mg)	$\Delta H^*_{obs.}$ (kJ mol^{-1})	n	$\Delta H^*_{dec.}$ (kJ mol^{-1})	$\Delta H^{298}_{dec.}$ (kJ mol^{-1})
506	4.905	10.065	190	2.39	300	238
507	2.580	10.630	145	2.84	276	213
515	4.095	11.025	150	2.67	272	207
516	4.060	12.065	159	2.34	266	201

Mean $\Delta H^{298}_{dec.}$ = 215.0 kJ mol^{-1}

$$[W(CO)_3(NCCH_3)_3](c,298) \rightarrow$$

$$3CH_3CN(g,T) + xW(c,T) + (1-x)W(CO)_6(g,T) + 3(2x-1)CO(g,T) \qquad (8)$$

of the metal deposited in the reaction vessel in thermal decomposition studies at 460 K (vacuum sublimation technique) indicated values $x \sim 0.6$—0.7 at this temperature.

At the lower temperature range, the limiting value $x = 0.5$ is more likely to be approached, and with this value, $\Delta H^{394}_{dec.} \sim 223$ kJ mol^{-1} (which reduces to $\Delta H^{298}_{dec.} \sim 195$ kJ mol^{-1}) for the partial decomposition at 298 K (eq. 9) leads to

$$[W(CO)_3(NCCH_3)_3](c) \rightarrow 3CH_3CN(g) + 1/2\ W(c) + 1/2\ W(CO)_6(g) \qquad (9)$$

$\Delta H_f^\circ[W(CO)_3(NCCH_3)_3, c] \geqslant -415.7$ kJ mol^{-1}.

Measurements of the heat of iodination were made at temperatures in the range 506—516 K, but the results obtained (Table 8) were somewhat erratic. The mean $\Delta H^{298}_{dec.} = 215.0$ kJ mol^{-1}, presumed to refer to total decomposition ($x = 1.0$) corresponds to $\Delta H_f^\circ[W(CO)_3(NCCH_3)_3, c] = -325$ kJ mol^{-1}. This value appears high by comparison both with that from partial thermal decomposition, and with that reported by Bleijerveld and Vrieze [5] from ligand displacement studies.

Discussion

The present results are summarized in Table 9 in terms of the derived enthalpies of formation, $\Delta H_f^\circ(c)$.

The measurement of the heat of sublimation of the compounds discussed here poses special problems, since they all undergo partial decomposition at temperatures above about 390 K, even when a mild vacuum (0.1 Torr) is applied. This decomposition is rapid and complete at higher temperatures (>450 K), or when a more rigorous vacuum (10^{-3} Torr) is applied to the sample at the lower (390 K) temperature. In order to circumvent this problem we have estimated values of the heats of sublimation in the following manner, taking *fac*-$[Mo(CO)_3py_3]$ as an example. We write the formula as $\{[Mo(CO)_3(NCH)_3] \cdot [(CH{=}CH)_{12}]\}$. The part $[Mo(CO)_3(NCH)_3]$ is considered equivalent to $Mo(CO)_6$ ($\Delta H_{sub} \sim 74$ kJ mol^{-1}) and the part $[(CH{=}CH)_{12}]$ adds to this by $2\Delta H_{vap.}(C_6H_6)$ 68 kJ mol^{-1}, giving the estimated heat of sublimation of crystalline *fac*-$[Mo(CO)_3py_3]$ as 142 kJ mol^{-1}. Table 10 lists chosen $\Delta H_f^\circ(c)$ values, together with estimates of the heats of sublimation of the crystalline complexes; the final columns give the

TABLE 9

STANDARD ENTHALPIES OF FORMATION

Compound	$\Delta H_f^\circ(c)$ (kJ mol^{-1})	Method
fac-$[Mo(CO)_3py_3]$	⩽—229 ⩾—289	TD/VS
	—(275 ± 8)	ΔH(synthesis)
fac-$[W(CO)_3py_3]$	⩽—222	TD/VS
	—(250 ± 9)	ΔH(synthesis)
cis-$[Cr(CO)_4py_2]$	⩾—515	TD/VS
fac-$[Mo(CO)_3(NCCH_3)_3]$	⩾—409	TD/VS
	—(410 ± 10)	Iodination
fac-$[W(CO)_3(NCCH_3)_3]$	⩾—416	TD/VS
	—(325)	Iodination
	—(405)	Ref. 5.

values of $\Delta H_f^\circ(g)$ and $\Delta H_{disrupt}^{298}$, the latter referring to disruption in the gaseous phase as indicated by eq. 10 for molecules $[M(CO)_3L_3]$ (L = py, MeCN; M = Mo, W), and to eq. 10a for $[M(CO)_4L_2]$ (L = py, M = Cr).

$$[M(CO)_3L_3](g) \rightarrow 3L(g) + 3CO(g) + M(g) \qquad (10)$$

$$[M(CO)_4L_2](g) \rightarrow 2L(g) + 4CO(g) + M(g) \qquad (10a)$$

The bond-enthalpy contributions, D(L—M), for (L = py; M = Cr, Mo, W) and (L = MeCN; M = Mo, W) may be evaluated from $\Delta H_{disrupt.}$ accepting that the bond-enthalpy contributions, D(M—CO) remain unchanged from the mean values, in the hexacarbonyls. These are shown in Table 11, and the results indicate that the ligands CO, pyridine and acetonitrile have similar bond enthalpy contributions to a given metal. In that these values depend on estimated heats of sublimation, the trend D(M—CO) > D(M—py) > D(M—NCMe) may not necessarily hold true. The value given for D(py—Cr) should be regarded as provisional, and requires confirmation from studies other than thermal decomposition alone.

These conclusions are in particular contrast to those of Vrieze and coworkers [4,5] who find D(W—NCMe) 185 kJ mol^{-1} in *fac*-$[W(CO)_3(NCMe)_3]$ and D(W—py) 254 kJ mol^{-1} in $[W(CO)_5py]$. We believe that a major source of this disagreement lies in the heats of sublimation. Vrieze reports [4,5] directly measured values of $\Delta H_{sub}[W(CO)_3(CNMe)_3]$ 43.9 kJ mol^{-1} and $\Delta H_{sub.}[W(CO)_5py]$ 30.5 kJ mol^{-1}.

TABLE 10

$\Delta H_f^\circ(g)$ AND $\Delta H_{disrupt.}$ VALUES

Compound	$\Delta H_f^\circ(c)$ (kJ mol^{-1})	$\Delta H_{sub.}$ (kJ mol^{-1})	$\Delta H_f^\circ(g)$ (kJ mol^{-1})	$\Delta H_{disrupt.}^{298}$ (kJ mol^{-1})
fac-$[Mo(CO)_3py_3]$	—(275 ± 12)	~142	—133	898
fac-$[W(CO)_3py_3]$	—(250 ± 12)	~146	—104	1057
cis-$[Cr(CO)_4py_2]$	—(505 ± 20)	~117	—388	632
fac-$[Mo(CO)_3(NCCH_3)_3]$	—(410 ± 12)	~96	—314	862
fac-$[W(CO)_3(NCCH_3)_3]$	—(405 ± 12)	~100	—305	1045

TABLE 11

BOND ENTHALPY CONTRIBUTIONS, D(M—L) (kJ mol^{-1})

L	M = Cr	M = Mo	M = W
CO	107	152	179
py	102	146	173
MeCN		135	169

We recall that $\Delta H_{\text{sub.}}$[W(CO)$_6$] 76.6 kJ mol^{-1} and that several derivatives of metal carbonyls show [7] values of $\Delta H_{\text{sub.}}$ in the range 100—150 kJ mol^{-1}, so that the values reported by Vrieze appear to be unexpectedly low. Moreover, values in the range 30—50 kJ mol^{-1} would normally be associated with vaporisation of volatile liquids (e.g. $\Delta H_{\text{vap.}}$(acetone) 30.96; $\Delta H_{\text{vap.}}$(pyridine) 40.21; $\Delta H_{\text{vap.}}$(acetonitrile) 33.4 kJ mol^{-1}); the heat of sublimation of iodine is 62.34 kJ mol^{-1}.

The results we have obtained are contrary to the surprising trend D(W—py) > D(W—NCMe) > D(W—CO) described by Vrieze [4,5]. Our results are consistent with the differences in the σ- and π-bonding capabilities of the various ligands, as detected by other physical measurements, in suggesting that an increase in the π-bonding component of the metal ligand bond results in a slight increase in the bond enthalpy contribution. Our results provide further evidence for a comparison between D(M—CO) and D(M—py) as outlined in the Introduction [1,2] which may not be very sensitive to formal oxidation state. In turn, this may be used as an index of the (Cu—CO) bond enthalpy contribution, since D(Cu—3-bromopyridine) has been estimated [2] as 142 kJ mol^{-1}. Carbon monoxide complexes of copper have been identified in low temperature matrices [17] and also in systems such [18] as [Cu(CO){HB(pz)$_3$}].

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