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VAPOUR PRESSURE MEASUREMENTS ON $M(CO)_5L$ (M = Cr, Mo, W; L = PIPERIDINE, PYRIDINE, PYRAZINE, PYRAZOLE, THIAZOLE)

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ABSTRACT

The vapour pressures and enthalpies of sublimation for a number of $M(CO)_5L$-complexes (M = Cr, Mo, W and L = piperidine, pyridine, pyrazine, pyrazole, thiazole) have been determined by the Knudsen effusion method. The results are compared with similar complexes and dipole moment measurements from the literature.

INTRODUCTION

Part of the research in this laboratory is concerned with the determination of the heat of substitution of $M(CO)_{6-x}L_x$ (M = Cr, Mo, W and L = nitrogen-donor ligand) by CO [1—3]. Accurate enthalpies of sublimation are needed to calculate the reaction enthalpies in the gas phase and to derive the metal—nitrogen bond energy.

Enthalpies of sublimation measured previously with an automatic apparatus, using the static method with an elastic membrane manometer, which was developed in this laboratory [4] have been subject to criticism [5]. A disadvantage of this static method is the accumulation of decomposed materials when thermally unstable compounds are used. Recently a Knudsen effusion cell has been constructed [6] by which low vapour pressures and enthalpies of sublimation can be determined by an alternative dynamic method.

In this paper we report the vapour pressures and the enthalpies of sublimation for a number of $M(CO)_5L$ complexes, where L is piperidine, pyridine, pyrazine, pyrazole and thiazole.

EXPERIMENTAL

The complexes were synthesized according to literature methods [2,3,7,8]. The purity was checked by elemental analysis and IR spectra of the carbonyl stretching region. In some cases the presence of traces of hexa-

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carbonyl could not be avoided, which resulted in a higher weight loss during the first hours of the measurements.

The thermochemical measurements were made using a Mettler Thermoanalyser type 1 with a Knudsen effusion cell placed on the balance. The installation and construction of the Knudsen cell have been published elsewhere [6,9].

The equilibrium vapour pressures were calculated with the aid of the Knudsen equation

$$p = \frac{\Delta m}{\Delta t} \times \frac{1}{q} \sqrt{\frac{2\pi RT}{M}}$$

where p = vapour pressure, $\Delta m/\Delta t$ = rate of weight loss, q = calibrated orifice area, R = gas constant, T = absolute temperature and M = molecular weight. The temperature was kept constant to ±0.1 K and the accuracy in $\Delta m/\Delta t$ was about 1×10^{-12} kg sec^{-1}. The diameters of the orifice were 0.1 and 3 mm. The orifice calibration has been published elsewhere [6,10].

For each set of data a curve was fitted according to

$$\ln p = -\frac{A}{T} + B$$

and the enthalpy of sublimation was calculated from A. A least-squares analysis afforded a standard deviation for the ΔH values.

RESULTS AND DISCUSSION

The existence of most complexes in the vapour phase has been established by photoelectron spectroscopy [7,8]. Also, mass spectra have been published [11] and matrix isolation IR and UV spectroscopy has been employed [12] successfully for some of the compouds. The temperature range is, however, limited by decomposition at elevated temperatures. The reproducibility was continuously checked by measuring at temperatures in a random fashion.

The measured vapour pressures and enthalpies of sublimation of the complexes are presented in Table 1 and shown graphically in Fig. 1.

Additionally, the vapour pressures and enthalpies of sublimation of the hexacarbonyls have been determined. The results of the hexacarbonyls are presented in Table 2. $Cr(CO)_6$ and $W(CO)_6$ agree very well with previous work confirming the accuracy of our measurements (see ref. 13 for a detailed survey). The sublimation enthalpy of $Mo(CO)_6$ is some 4 kJ mole^{-1} higher, however.

For some of the complexes experimental dipole moments have been reported [14]. In Fig. 2 these dipole moments have been plotted against the enthalpies of sublimation. It is seen that generally the enthalpy increases with an increase of dipole moment. Within a series of $M(CO)_5L$ with the same ligand L the magnitude of the sublimation enthalpy is $Cr \leqslant Mo \leqslant W$ in analogy with the hexacarbonyls. On the other hand, this trend may also be attributed to the relative dipole moments.

TABLE 1

Vapour pressure and enthalpies of sublimation of $M(CO)_5L$

Sample	Temp. (K)	Wt. loss (kg sec^{-1})	Pressure (Nm^{-2})	$\ln p = -\frac{A}{T} + B$	ΔH^{subl} (kJ mole^{-1})
$Cr(CO)_5$piperidine **	264.9	5×10^{-12}	0.4×10^{-3}	$A = 1.12 \times 10^4$	93.5
$M = 277.202$	270.3	8×10^{-12}	0.7×10^{-3}	$B = 34.5$	± 1.9
	270.0	10×10^{-12}	0.8×10^{-3}		
	278.6	32×10^{-12}	2.9×10^{-3}		
	282.4	62×10^{-12}	5.6×10^{-3}		
	285.9	86×10^{-12}	7.8×10^{-3}		
	288.1	129×10^{-12}	11.7×10^{-3}		
	290.2	150×10^{-12}	13.7×10^{-3}		
	292.4	224×10^{-12}	20.6×10^{-3}		
	295.7	335×10^{-12}	30.9×10^{-3}		
	298.1	438×10^{-12}	40.6×10^{-3}		
$Mo(CO)_5$piperidine **	274.6	2×10^{-12}	0.2×10^{-3}	$T = 274.6—288.6$	121.9
$M = 321.142$	276.9	4×10^{-12}	0.3×10^{-3}	$A = 1.47 \times 10^4$	± 5.1
	280.1	6×10^{-12}	0.5×10^{-3}	$B = 44.8$	
	283.1	11×10^{-12}	1.0×10^{-3}		
	285.1	14×10^{-12}	1.2×10^{-3}	$T = 287.1—305.7$	94.5
	287.1	24×10^{-12}	2.0×10^{-3}	$A = 1.14 \times 10^4$	± 2.9
	287.9	27×10^{-12}	2.3×10^{-3}	$B = 33.3$	
	288.6	25×10^{-12}	2.1×10^{-3}		
	291.7	42×10^{-12}	3.6×10^{-3}		
	293.5	56×10^{-12}	4.8×10^{-3}		
	295.7	61×10^{-12}	5.3×10^{-3}		
	297.7	93×10^{-12}	8.0×10^{-3}		
	302.0	155×10^{-12}	13.4×10^{-3}		
	305.7	251×10^{-12}	21.8×10^{-3}		
$W(CO)_5$piperidine **	288.9	4×10^{-12}	0.3×10^{-3}	$A = 1.28 \times 10^4$	106.4
$M = 409.052$	291.4	6×10^{-12}	0.4×10^{-3}	$B = 36.2$	± 1.0
	295.9	12×10^{-12}	0.9×10^{-3}		
	298.7	19×10^{-12}	1.5×10^{-3}		
	305.2	43×10^{-12}	3.3×10^{-3}		
	307.7	63×10^{-12}	4.9×10^{-3}		
	310.6	88×10^{-12}	6.8×10^{-3}		
	312.5	111×10^{-12}	8.7×10^{-3}		
	322.0	357×10^{-12}	28.3×10^{-3}		
	326.5	623×10^{-12}	49.7×10^{-3}		
$Cr(CO)_5$pyridine *	293.7	4×10^{-12}	0.1×10^{-1}	$A = 1.24 \times 10^4$	103.2
$M = 271.152$	298.1	8×10^{-12}	0.3×10^{-1}	$B = 38.0$	± 1.8
	310.3	43×10^{-12}	1.4×10^{-1}		
	315.5	76×10^{-12}	2.5×10^{-1}		
	316.6	84×10^{-12}	2.8×10^{-1}		
$Mo(CO)_5$pyridine **	282.6	19×10^{-12}	1.6×10^{-3}	$A = 1.23 \times 10^4$	102.0
$M = 315.092$	283.1	20×10^{-12}	1.7×10^{-3}	$B = 37.3$	± 2.0
	286.7	38×10^{-12}	3.2×10^{-3}		
	290.9	66×10^{-12}	5.7×10^{-3}		
	295.2	116×10^{-12}	10.0×10^{-3}		
	298.9	204×10^{-12}	17.8×10^{-3}		

TABLE 1 (*continued*)

Sample	Temp. (K)	Wt. loss (kg sec^{-1})	Pressure (Nm^{-2})	$\ln p = -\frac{A}{T} + B$	ΔH^{subl} (kJ mole^{-1})
W(CO)$_5$pyridine **	284.6	3×10^{-12}	0.2×10^{-3}	$A = 1.32 \times 10^4$	109.7
M = 403.002	287.1	3×10^{-12}	0.3×10^{-3}	$B = 37.9$	± 2.7
	290.9	8×10^{-12}	0.6×10^{-3}		
	291.4	8×10^{-12}	0.6×10^{-3}		
	298.1	23×10^{-12}	1.7×10^{-3}		
	298.7	26×10^{-12}	2.0×10^{-3}		
	300.7	32×10^{-12}	2.5×10^{-3}		
	300.7	35×10^{-12}	2.7×10^{-3}		
	303.9	56×10^{-12}	4.3×10^{-3}		
	306.2	73×10^{-12}	5.7×10^{-3}		
	313.0	170×10^{-12}	13.4×10^{-3}		
Cr(CO)$_5$pyrazine *	294.2	4×10^{-12}	0.1×10^{-1}	$A = 1.20 \times 10^4$	99.7
M = 272.14	295.7	5×10^{-12}	0.2×10^{-1}	$B = 36.5$	± 3.0
	302.7	15×10^{-12}	0.5×10^{-1}		
	306.2	26×10^{-12}	0.8×10^{-1}		
	311.1	42×10^{-12}	1.4×10^{-1}		
	311.3	36×10^{-12}	1.2×10^{-1}		
	315.3	68×10^{-12}	2.2×10^{-1}		
	318.2	64×10^{-12}	2.2×10^{-1}		
	319.2	113×10^{-12}	3.8×10^{-1}		
	324.5	192×10^{-12}	6.5×10^{-1}		
	328.1	301×10^{-12}	10.2×10^{-1}		
	334.3	517×10^{-12}	17.7×10^{-1}		
W(CO)$_5$pyrazine **	287.1	5×10^{-12}	0.4×10^{-3}	$A = 1.30 \times 10^4$	108.4
M = 403.99	289.4	8×10^{-12}	0.6×10^{-3}	$B = 37.6$	± 1.3
	294.7	16×10^{-12}	1.2×10^{-3}		
	295.7	18×10^{-12}	1.4×10^{-3}		
	300.2	36×10^{-12}	2.8×10^{-3}		
	303.1	54×10^{-12}	4.2×10^{-3}		
	307.8	104×10^{-12}	8.1×10^{-3}		
	311.8	186×10^{-12}	14.6×10^{-3}		
	316.3	325×10^{-12}	25.7×10^{-3}		
	320.5	560×10^{-12}	44.5×10^{-3}		
Cr(CO)$_5$pyrazole **	270.0	10×10^{-12}	0.9×10^{-3}	$A = 1.06 \times 10^4$	88.4
M = 206.102	275.4	24×10^{-12}	2.2×10^{-3}	$B = 32.5$	± 1.8
	279.9	48×10^{-12}	4.4×10^{-3}		
	281.1	59×10^{-12}	5.5×10^{-3}		
	283.9	76×10^{-12}	7.1×10^{-3}		
	286.1	115×10^{-12}	10.7×10^{-3}		
	290.7	191×10^{-12}	18.0×10^{-3}		
	295.2	305×10^{-12}	29.0×10^{-3}		
	297.7	385×10^{-12}	36.8×10^{-3}		
	302.9	762×10^{-12}	73.4×10^{-3}		

TABLE 1 (*continued*)

Sample	Temp. (K)	Wt. loss (kg $\sec^{-1}$)	Pressure (Nm^{-2})	$\ln p = -\frac{A}{T} + B$	ΔH^{subl} (kJ $mole^{-1}$)
W(CO)$_5$pyrazole **	287.4	4×10^{-12}	0.3×10^{-3}	$A = 1.35 \times 10^4$	112.5
$M = 391.982$	290.1	5×10^{-12}	0.4×10^{-3}	$B = 38.9$	± 2.4
	295.4	10×10^{-12}	0.8×10^{-3}		
	300.7	29×10^{-12}	2.3×10^{-3}		
	302.0	37×10^{-12}	2.9×10^{-3}		
	307.0	72×10^{-12}	5.7×10^{-3}		
	313.4	180×10^{-12}	14.4×10^{-3}		
	317.7	320×10^{-12}	25.7×10^{-3}		
	318.2	342×10^{-12}	27.5×10^{-3}		
	323.0	568×10^{-12}	46.1×10^{-3}		
	327.2	867×10^{-12}	70.7×10^{-3}		
Cr(CO)$_5$thiazole **	270.0	7×10^{-12}	0.6×10^{-3}	$A = 1.23 \times 10^4$	102.0
$M = 277.182$	270.5	10×10^{-12}	0.9×10^{-3}	$B = 38.3$	± 2.7
	276.1	28×10^{-12}	2.5×10^{-3}		
	280.6	51×10^{-12}	4.6×10^{-3}		
	282.9	63×10^{-12}	5.7×10^{-3}		
	283.6	82×10^{-12}	7.4×10^{-3}		
	288.1	133×10^{-12}	12.1×10^{-3}		
	289.4	165×10^{-12}	15.1×10^{-3}		
	292.7	329×10^{-12}	30.2×10^{-3}		
	296.9	483×10^{-12}	44.6×10^{-3}		
	300.9	814×10^{-12}	75.7×10^{-3}		

* Orifice diameter 0.1 mm.
** Orifice diameter 3 mm.

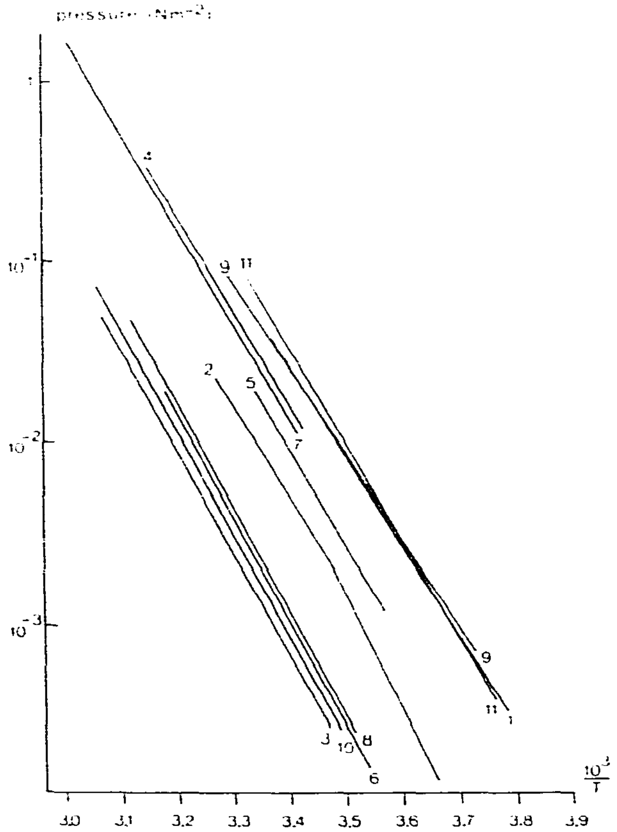
The sublimation enthalpies of M(CO)$_5$L (L = N-donor ligand) are much larger than the corresponding PX$_3$ (X = F, Cl, Br) complexes [10]. Indeed the smaller σ-donation in combination with the higher π-back bonding of PX$_3$ will result in a smaller overall dipole moment and in enthalpy values close to the hexacarbonyls.

TABLE 2

A and *B* parameters and enthalpy of sublimation in kJ mole^{-1} of the group VI B hexacarbonyls

	A *	B *	ΔH^{subl}	Orifice diameter (mm)	Temp. range (K)
Cr(CO)$_6$	8610 ± 200	32.3	71.6 ± 1.7	0.1	240—280
Mo(CO)$_6$	9252 ± 106	34.0	76.9 ± 0.9	0.1	240—285
W(CO)$_6$	9489 ± 132	33.3	78.9 ± 1.1	0.1	250—292

* Pressure in Nm^{-2}, $\ln p = -\frac{A}{T} + B$.



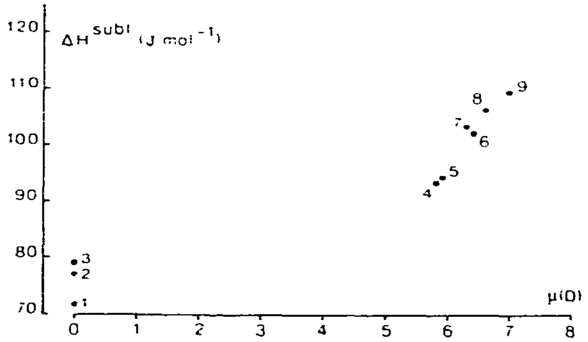


Fig. 1. Vapour pressures of the complexes: 1, $Cr(CO)_5$piperidine; 2, $Mo(CO)_5$piperidine; 3, $W(CO)_5$piperidine; 4, $Cr(CO)_5$pyridine; 5, $Mo(CO)_5$pyridine; 6, $W(CO)_5$pyridine; 7, $Cr(CO)_5$pyrazine; 8, $W(CO)_5$pyrazine; 9, $Cr(CO)_5$pyrazole; 10, $W(CO)_5$pyrazole; 11, $Cr(CO)_5$thiazole.

Fig. 2. Plot of the enthalpy of sublimation as a function of the dipole moment: 1, $Cr(CO)_6$; 2. $Mo(CO)_6$; 3, $W(CO)_6$; 4, $Cr(CO)_5$piperidine; 5, $Mo(CO)_5$piperidine; 6, $Mo(CO)_5$pyridine; 7, $Cr(CO)_5$pyridine; 8, $W(CO)_5$piperidine; 9, $W(CO)_5$pyridine.

For $Mo(CO)_5$piperidine two different slopes at temperatures below and above 288.8 K were observed. It is assumed a solid state transition occurs at this temperature.

Attempts to determine vapour pressures of bis-substituted hexacarbonyl complexes, in particular $M(CO)_4$piperidine$_2$ (M = Cr, W), failed. The compounds decomposed before any rate of weight loss could be detected. Vapour pressures of these compounds are too low to be measured by the Knudsen effusion method.

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