Thermochimica Acta, 42 (1980) 315—321
Elsevier Scientific Publishing Company, Amsterdam — Printed in Belgium

VAPOUR PRESSURE MEASUREMENTS ON $M(CO)_5L$ COMPLEXES ($M = Cr, W; L = CO, P(O\emptyset)_3, P\emptyset_3, PMe_3, NMe_3$ AND PYRIDAZINE)

G. BOXHOORN, J.M. ERNSTING, D.J. STUFKENS and A. OSKAM *

Anorganisch Chemisch Laboratorium, J.H. van 't Hoff Instituut, Nieuwe Achtergracht 166, 1018 WV Amsterdam (The Netherlands)

(Received 10 June 1980)

ABSTRACT

By means of the Knudsen effusion method the vapour pressures and enthalpies of sublimation of $M(CO)_5L$ ($M = Cr, W; L = Co, P(O\emptyset)_3, P\emptyset_3, PMe_3, NMe_3$ and pyridazine were determined and compared with their dipole moments.

INTRODUCTION

Vapour pressure measurements have been carried out on a number of $M(CO)_5L$ ($M = Cr, Mo, W; L = PF_3, PCl_3, PBr_3$, piperidine, pyridine, pyrazine, pyrazole and thiazole) and $M(CO)_{6-x}L_x$ ($M = W; L = CH_3CN; x = 1—3$) complexes in our laboratory [1—3]. The Knudsen effusion method has proved to be the most reliable for measuring vapour pressures for these types of complexes [1—3].

In this paper we report the vapour pressures of $M(CO)_5L$ complexes ($M = Cr, W; L = CO, P(O\emptyset)_3, P\emptyset_3, PMe_3, NMe_3$ and pyridazine) measured by the Knudsen method. The enthalpies of sublimation determined from the vapour pressure data are compared with the dipole moments of the corresponding complexes.

EXPERIMENTAL

The $M(CO)_5L$ complexes were prepared using standard literature methods. The $M(CO)_5L$ ($M = Cr, W; L = P(O\emptyset)_3$ and $P\emptyset_3$) complexes were synthesized according to the method of Magee et al. [4] (by adding the ligand to the corresponding hexacarbonyl in refluxing diglyme; the diglyme is removed under reduced pressure and excess hexacarbonyl by vacuum sublimation). The $M(CO)_5PMe_3$ complexes were prepared using the method of Connor et al. [5] (by adding $AgNO_3PMe_3$ to $[M(CO)_5Cl]$-Et_4N in a CH_2Cl_2 solution). The $M(CO)_5NMe_3$ compounds ($M = Cr, W$) were prepared under a nitrogen atmo-

---

* To whom correspondence should be addressed.

sphere (a suspension of $ONMe_3$ was added to $M(CO)_6$ in freshly distilled tetrahydrofuran at −50°C, as described by Koelle [6]). The preparation of $M(CO)_5$pyridazine is described in ref. 7. $M(CO)_6$ (M = Cr, Mo, W) complexes were purchased from Strem Chemicals and used without further purification. The purity of the complexes was checked by IR spectroscopy and microanalysis. A detailed description of the equipment is given in refs. 8 and 9. The diameters of the cell orifices employed were 0.1 and 3 mm, respectively; their calibration has been published elsewhere [1,9]. The sample weights varied between 100 and 200 mg and the vapour pressures were calculated according to the Knudsen equation

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

where p = vapour pressure, R = gas constant, $\Delta m/\Delta t$ = rate of weight loss, T = temperature, q = calibrated orifice area, and M = molecular weight. The accuracy in $\Delta m/\Delta t$ was 1×10^{-12} kg sec^{-1} and in the temperature ±0.1 K.

$$\ln p = -\frac{A}{T} + B \tag{2}$$

Enthalpies of sublimation were calculated from eqn. (2). A least squares analysis of the data afforded the standard deviation quoted. The reproducibility of the measurements was checked by arbitrary fluctuation of the temperatures. Attempts to obtain vapour pressure data for $Cr(CO)_5P(O\phi)_3$ failed. Dipole moments were measured on a General Radio Capacitance Measuring Assembly type 1620-A.

RESULTS AND DISCUSSION

For vapour pressure measurements it is necessary to prove the existence of the complexes in the vapour phase, since some $M(CO)_5L$ complexes possess a low thermodynamic stability. All complexes reported here have been the subject of matrix isolation and photoelectron spectroscopy studies [7,10—15], and from these studies it has been concluded that the $M(CO)_5L$ complexes (M = Cr; W; L = $P(O\phi)_3$, $P\phi_3$, PMe_3 and NMe_3) exist in the vapour phase.

In order to inspect the reliability of the Knudsen cell apparatus the enthalpies of sublimation of $M(CO)_6$ (M = Cr, Mo, W) complexes were measured (see Table 1).The data for the $M(CO)_6$ complexes are in agreement with previously reported data [16]. Figures 1 and 2 show the vapour pressure curves of the $M(CO)_6$ and $M(CO)_5L$ complexes, respectively.

The enthalpies of sublimation of the $M(CO)_6$ complexes follow the order $Cr < Mo < W$. This order is also generally found for the corresponding $M(CO)_5L$ complexes with the exception of $M(CO)_5L$ (L = $P\phi_3$, PF_3 [1], PBr_3 [1], pyridine [2]). A general relationship between enthalpies of sublimation and dipole moments [17—19] was not found; some N-donor complexes did show a trend, whereas P-donor complexes did not, as is demonstrated in Table 2.

TABLE 1

Vapour pressures and enthalpies of sublimation of $M(CO)_5X$

Sample	Temp. (K)	Weight loss × 10^{12} (kg sec^{-1})	Pressure (Pa)	$\ln p = -\frac{A}{T} + B$	ΔH_s (kJ $mole^{-1}$)
$Cr(CO)_6$ [a]	240.6	9	0.3 (×10^{-1})	$A = 8610$	$\Delta H_s = 71.6 \pm 1.7$
	244.7	14	0.5	$B = 32.2$	$\Delta H_s = 71.8 \pm 0.4$
$M = 220.062$	247.4	26	0.9		[16]
	250.6	43	1.4		
	252.5	52	1.7		
	257.4	72	2.4		
	260.0	115	3.9		
	263.3	163	5.5		
	264.9	249	8.4		
	269.3	380	13.0		
	271.6	529	18.2		
	280.2	1318	45.9		
$Mo(CO)_6$ [a]	243.6	7	0.2 (×10^{-1})	$A = 9252$	$\Delta H_s = 76.9 \pm 0.9$
	247.4	12	0.4	$B = 34.0$	
$M = 264.002$	257.4	47	1.4		$\Delta H_s = 73.8 \pm 1.0$
	257.6	53	1.6		[16]
	261.0	77	2.4		
	265.4	129	4.0		
	268.0	204	6.4		
	272.1	341	10.7		
	275.8	478	15.1		
	283.7	1378	44.1		
$W(CO)_6$ [a]	250.3	4	0.1 (×10^{-1})	$A = 9489$	$\Delta H_s = 78.9 \pm 1.1$
	251.1	4	0.09	$B = 33.3$	
$M = 351.913$	255.5	9	0.2		$\Delta H_s = 76.5 \pm 1.3$
	257.6	11	0.3		[16]
	259.8	16	0.4		
	260.7	19	0.5		
	260.7	14	0.4		
	264.7	27	0.7		
	265.5	32	0.9		
	270.1	59	1.6		
	273.3	89	2.4		
	274.4	106	2.9		
	281.1	238	6.6		
	281.1	234	6.5		
	285.6	406	11.3		
	285.9	381	10.6		
	292.0	721	20.3		
$W(CO)_5P(O\phi)_3$ [b]	308.1	6	0.3 (×10^{-3})	$A = 14460$	$\Delta H_s = 120.2 \pm 6.6$
	310.8	9	0.6	$B = 38.8$	
$M = 634.193$	312.8	8	0.5		
	315.5	14	0.6		
	316.7	10	0.9		
	318.9	17	1.1		
	325.1	59	3.8		
	327.5	100	6.5		
	334.2	121	7.9		
	337.4	194	12.8		
	341.7	751	49.8		
	348.7	933	62.5		

TABLE 1 (continued)

Sample	Temp. (K)	Weight loss × 10^{12} (kg $\sec^{-1}$)	Pressure (Pa)	$\ln p = -\frac{A}{T} + B$	ΔH_s (kJ mole^{-1})
$Cr(CO)_5P\phi_3$ [b]	324.4	7	0.5 (×10^{-3})	$A = 20480$	$\Delta H_s = 170.2 \pm 6.8$
	330.4	21	1.6	$B = 55.5$	
$M = 454.344$	334.0	40	3.1		
	337.1	70	5.4		
	343.1	165	13.0		
	346.7	442	34.0		
$W(CO)_5P\phi_3$ [b]	339.8	16	1.1 (×10^{-3})	$A = 19509$	$\Delta H_s = 162.2 \pm 8.3$
	343.9	38	2.6	$B = 50.7$	
$M = 586.194$	346.5	53	3.7		
	348.2	78	5.5		
	348.7	89	6.2		
	349.4	63	4.4		
	350.1	78	5.5		
	351.3	138	9.7		
	351.8	153	10.7		
	352.3	115	8.1		
	355.6	245	17.2		
	358.8	396	28.0		
	363.6	635	45.2		
$Cr(CO)_5PMe_3$ [a]	267.4	13	0.4 (×10^{-1})	$A = 10976$	$\Delta H_s = 91.2 \pm 1.6$
	268.1	18	0.5	$B = 37.9$	
$M = 268.129$	277.0	54	1.7		
	277.7	59	1.9		
	279.8	87	2.8		
	283.8	158	5.0		
	288.0	254	8.1		
	288.1	273	8.8		
	291.7	414	13.3		
	296.0	681	22.1		
$W(CO)_5PMe_3$ [a]	283.1	4	0.1 (×10^{-1})	$A = 11282$	$\Delta H_s = 93.8 \pm 1.5$
	288.0	8	0.2	$B = 35.3$	
$M = 399.981$	290.2	9	0.2		
	300.4	36	1.0		
	302.9	60	1.6		
	308.3	97	2.6		
	313.1	186	5.1		
	317.7	281	7.7		
	322.9	504	14.0		
	327.0	756	21.1		
$Cr(CO)_5NMe_3$ [a]	248.4	1	0.04 (×10^{-1})	$A = 9652$	$\Delta H_s = 80.2 \pm 0.7$
	259.4	6	0.2	$B = 33.3$	
$M = 251.164$	268.0	19	0.6		
	278.5	77	2.5		
	280.5	102	3.3		
	283.8	143	4.7		
	287.7	234	7.7		
	288.0	242	8.0		
	292.2	389	13.0		

TABLE 1 (continued)

Sample	Temp. (K)	Weight loss × 10^{12} (kg sec^{-1})	Pressure (Pa)	ln $p = -\frac{A}{T} + B$	ΔH_s (kJ mole^{-1})
$W(CO)_5NMe_3$ [a]	279.3	5	0.1 (×10^{-1})	A = 10712	ΔH_s = 89.1 ± 2.1
	283.0	8	0.2	B = 33.9	
M = 383.014	286.5	10	0.3		
	291.0	22	0.6		
	299.7	62	1.7		
	303.6	109	3.0		
	307.9	167	4.6		
	313.0	290	8.1		
	316.0	393	11.0		
	320.8	491	13.9		
$W(CO)_5$pyridazine [b]	287.7	8	0.06 (×10^{-2})	A = 1280	ΔH_s = 106.4 ± 2.5
	291.7	16	0.1	B = 37.2	
M = 403.992	295.2	29	0.2		
	299.5	62	0.5		
	304.2	91	0.7		
	308.1	190	1.5		
	313.2	325	2.6		
	317.9	607	4.8		
	323.1	1017	8.1		

[a] Orifice diameter 0.1 mm.
[b] Orifice diameter 3 mm.

TABLE 2

Enthalpy of sublimation and dipole moments of $M(CO)_5L$ complexes

Molecule	ΔH_s (kJ mole^{-1})	μ (D)
$Cr(CO)_5$piperidine	93.5 [a]	5.8 [b]
$Mo(CO)_5$piperidine	94.5 [a]	5.9 [b]
$W(CO)_5$piperidine	106.4 [a]	6.6 [b]
$Cr(CO)_5$pyridine	103.2 [a]	6.3 [b]
$Mo(CO)_5$pyridine	102.0 [a]	6.4 [b]
$W(CO)_5$pyridine	109.7 [a]	7.0 [b]
$Cr(CO)_5PBr_3$	79.9 [c]	0.9 [d]
$Mo(CO)_5PBr_3$		0.8 [d]
$W(CO)_5PBr_3$	77.2 [c]	1.0 [d]
$Cr(CO)_5P\phi_3$	170.2	5.5 [e]
$Mo(CO)_5P\phi_3$		5.6 [f]
$W(CO)_5P\phi_3$	162.2	5.9 [e]

[a] Data from ref. 2.
[b] Data from ref. 17.
[c] Data from ref. 1
[d] Data from ref. 19.
[e] Measured in benzene solution.
[f] Data from ref. 18.

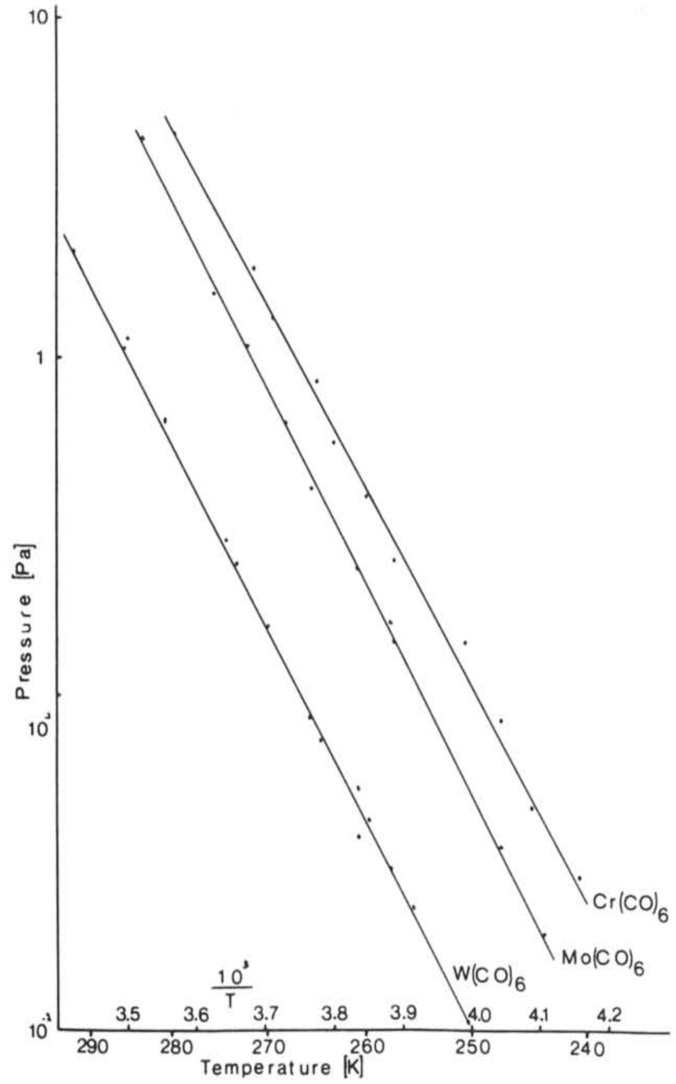

Fig. 1. Vapour pressure vs. temperature plots for the complexes (M(CO)$_6$ (M = Cr, Mo, W).

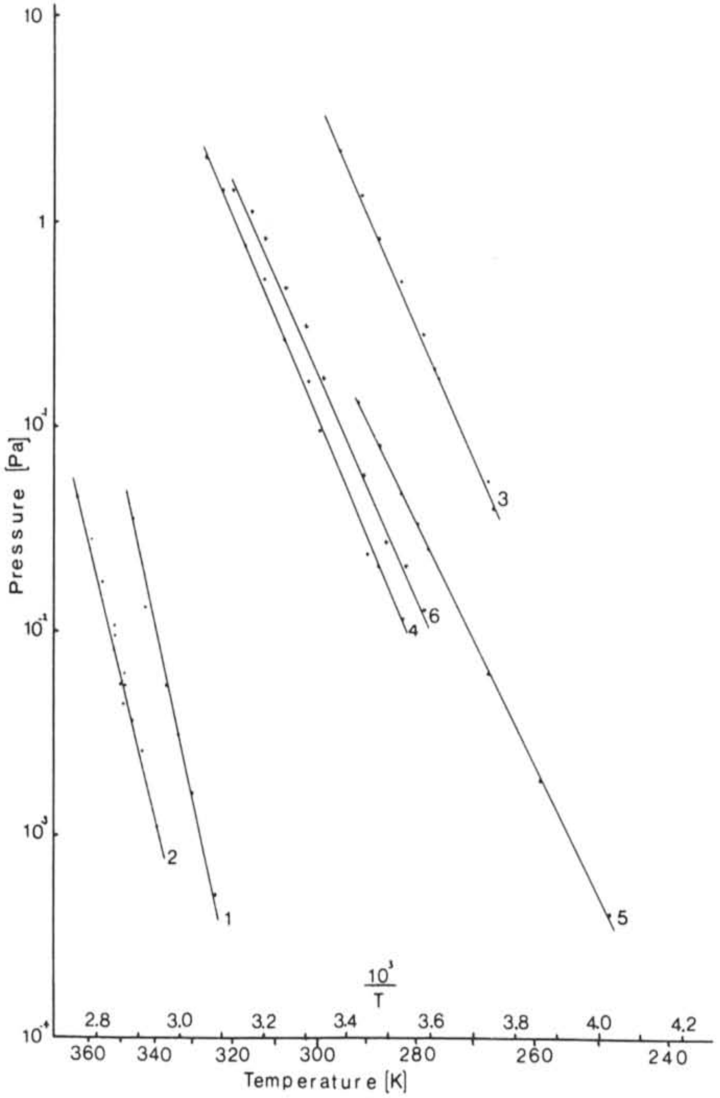

Fig. 2. Vapour pressure vs. temperature plots for the complexes: 1, $Cr(CO)_5P\varnothing_3$; 2, $W(CO)_5P\varnothing_3$; 3, $Cr(CO)_5PMe_3$; 4, $W(CO)_5PMe_3$; 5, $Cr(CO)_5NMe_3$; 6, $W(CO)_5NMe_3$.

The smaller dipole moments obtained for the $M(CO)_5PX_3$ (X = Br, Ø) complexes, which are expected for complexes with a decreasing σ-donation and an increasing π-backbonding, was not paralleled by smaller enthalpies of sublimation. Moreover, such a direct relation between μ and ΔH_S is not expected for these complexes containing ligands L, which will give strongly different intermolecular interaction.

ACKNOWLEDGEMENTS

Mr. J. Meijer is thanked for the measurement of the dipole moments and Mr. J. v.d. Helm for the preparation of some of the complexes.

REFERENCES

1 G. Boxhoorn, A.C. Jesse, J.M. Ernsting and A. Oskam, Thermochim. Acta, 27 (1978) 261.
2 H. Daamen, J.M. Ernsting and A. Oskam, Thermochim. Acta, 33 (1979) 217.
3 K.J. Cavell, J.M. Ernsting and D.J. Stufkens, 42 (1980) 343.
4 T.A. Magee, C.N. Matthews, T.S. Wang and J.H. Wotiz, J. Am. Chem. Soc., 83 (1961) 3200.
5 J.A. Connor, E.M. Jones and G.K. McEwen, J. Organometal, Chem., 43 (1972) 357.
6 U. Koelle, J. Organometal. Chem., 133 (1977) 53.
7 H. Daamen and A. Oskam, Inorg. Chim. Acta, 26 (1978) 81.
8 H.G. Wiedemann, Thermochim. Acta, 3 (1972) 355.
9 A.C. Jesse, J.M. Ernsting, D.J. Stufkens and K. Vrieze, Thermochim. Acta, 25 (1978) 69.
10 M.A. Graham, M. Poliakoff and J.J. Turner, J. Chem. Soc. A, (1971) 2939.
11 G. Boxhoorn, G.C. Schoemaker, D.J. Stufkens and A. Oskam, Inorg. Chim. Acta, 42 (1980) 241.
12 G. Boxhoorn, D.J. Stufkens and A. Oskam, J. Chem. Soc., Dalton Trans., (1980) 1328.
13 G. Boxhoorn, G.C. Schoemaker, D.J. Stufkens and A. Oskam, to be published.
14 H. Daamen, A. Oskam and D.J. Stufkens, Inorg. Chim. Acta, 38 (1980) 71.
15 B.R. Higginson, D.R. Lloyd, J.A. Connor and I.H. Hillier, J. Chem. Soc., Faraday Trans II, 70 (1974) 1418.
16 G. Pilcher, M.J. Ware and D.A. Pittman, J. Less-Common Metals, 42 (1975) and refs. therein.
17 W. Strohmeier und W. Langhaüser, Z. Phys. Chem. Neue Folge, 28 (1961) 268.
18 C. Barbeau and J. Turcotte, Can. J. Chem., 48 (1970) 3583.
19 E.O. Fischer and L. Knauss, Chem. Ber., 102 (1969) 223.