Thermochimica Acta, 27 (1978) 261–267

VAPOUR PRESSURE MEASUREMENTS ON $M(CO)_5PX_3$ (M = Cr, Mo, W; X = F, Cl, Br)

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(Received 7 January 1978)

ABSTRACT

The vapour pressures and the enthalpies of sublimation for the complexes $M(CO)_5PX_3$ (M = Cr, Mo, W; X = F, Cl, Br) were determined by the Knudsen effusion method. The monosubstituted complexes have comparable enthalpies of sublimation as have been found for the hexacarbonyls.

INTRODUCTION

In the course of a study of the photochemical behaviour of $M(CO)_5PX_3$ (M = Cr, Mo, W; X = F, Cl, Br) in Ar matrices at 10 K, it appeared to be necessary to know the vapour pressures of these carbonyl complexes with high accuracy[1]. Recently thermochemical investigations have been carried out in our laboratory on (acac)M-(substituted olefin)$_2$ and (acac)M(CO)$_2$; M = Rh(I), Ir(I)[2]. The vapour pressures and enthalpies of sublimation of these complexes were determined by the Knudsen effusion method, which technique has been shown to be suitable for complexes with low vapour pressures[2-4]. Therefore, in this paper we report the vapour pressures and the enthalpies of sublimation for the $M(CO)_5PX_3$ complexes, determined by the Knudsen effusion method.

EXPERIMENTAL

The $M(CO)_5PX_3$ complexes were synthesised, using standard literature methods [5-10] with slight modifications, as has been described in a previous paper[11].

The thermochemical measurements were made using a Mettler Thermoanalyser type 1, with a Knudsen cell placed on the balance. The installation and construction of the Knudsen cell has been published elsewhere[2, 3]. The diameters of the orifice were 0.1 and 1 mm and the sample weights varied between 100 and 200 mg.

The vacuum was better than 3×10^{-4} Pa and the temperature was kept

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constant to ± 0.1 K. The accuracy in $\Delta m/\Delta t$ was about 1×10^{-12} kg sec^{-1}. With the aid of the Knudsen equation (1)

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

where, p = vapour pressure, $\Delta m/\Delta t$ = rate of weight loss, q = calibrated orifice area, R = gas constant, T = temperature, M = molecular weight, the equilibrium vapour pressures were calculated. A plot of the temperature against ln pressure resulted in a curve according to eqn. (2)

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

The enthalpy of sublimation was calculated from this equation. The standard deviation for the ΔH values was determined by a least squares analysis. Benzoic acid, supplied by Mettler, was used as a standard.

RESULTS AND DISCUSSION

The orifice calibration of the Knudsen cell with an orifice diameter of 1 mm has been published by Jesse et al.[2]. For the Knudsen cell with a diameter of 0.1 mm, the calibration of the orifice area by measuring benzoic acid is given in Table 1. Only data (A, B) reported by Wiedemann[3] were used. Most of the $M(CO)_5PX_3$ complexes

TABLE 1

ORIFICE CALIBRATION OF THE KNUDSEN CELL

Benzoic acid *M = 122.12*[a]	*Temp.* *(K)*	*Weight loss* *(kg sec^{-1}) (× 10^{-12})*	*Pressure*[b] *(Pa) (× 10^{-1})*	*Orifice area* *(m^2) (× 10^{-9})*
	294.1	21	1.0	7.3
	294.9	23	1.1	7.3
	297.5	34	1.6	7.7
	298.7	37	1.8	7.4
	301.5	53	2.5	7.6
	305.2	72	3.8	6.9
	306.7	94	4.5	7.6
	308.1	112	5.2	7.8
	308.9	115	5.7	7.4
	312.5	168	8.4	7.4
	312.9	173	8.7	7.3
	315.3	217	11.3	7.1
	316.5	263	12.8	7.6
	316.5	260	12.8	7.5
	316.5	256	12.8	7.4
	320.6	397	19.4	7.6
	325.3	583	31.1	7.0

Orifice diameter 0.1 mm.
Mean value for q: $(7.4 \pm 0.3) \times 10^{-9}$ m^2.
[a] Molecular weight in g.
[b] Calculated with data from Wiedemann[3].

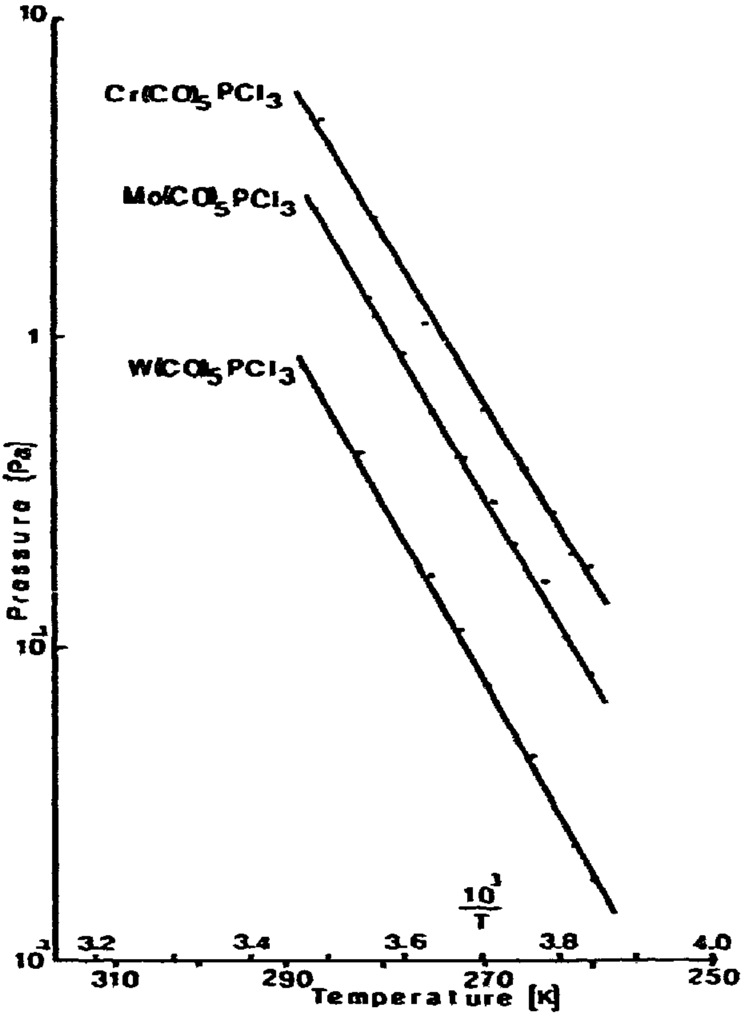

Fig. 1. Vapour pressures of the complexes Cr(CO)$_5$PCl$_3$; Mo(CO)$_5$PCl$_3$; W(CO)$_5$PCl$_3$.

have low thermodynamic stability. It is therefore necessary to investigate the existence of the complexes in the gas phase. From all M(CO)$_5$PX$_3$ molecules, photoelectron spectra were recorded with a volatile sample inlet system[11]. Recently, the IR/electronic matrix isolation spectra[3] were studied at 10 K. From these measurements and the photoelectron spectra it is deduced that these complexes exist in the gas phase and that decomposition does not occur. Vapour pressure measurements of Mo(CO)$_5$PBr$_3$, however, were not carried out, because partial decomposition could not be avoided.

The vapour pressure curves are shown in Figs. 1-3. The measured vapour pressures and enthalpies of sublimation of the complexes are compiled in Table 2.

The M(CO)$_5$PX$_3$ complexes have similar enthalpies of sublimation, as have been found for M(CO)$_6$ (Table 3, ref. 12a, b). The trends in the monosubstituted complexes and in the hexacarbonyls proved to be so irregular that, up till now, no explanation could be given for the behaviour of the enthalpies of sublimation. Therefore, further thermochemical measurements are needed.

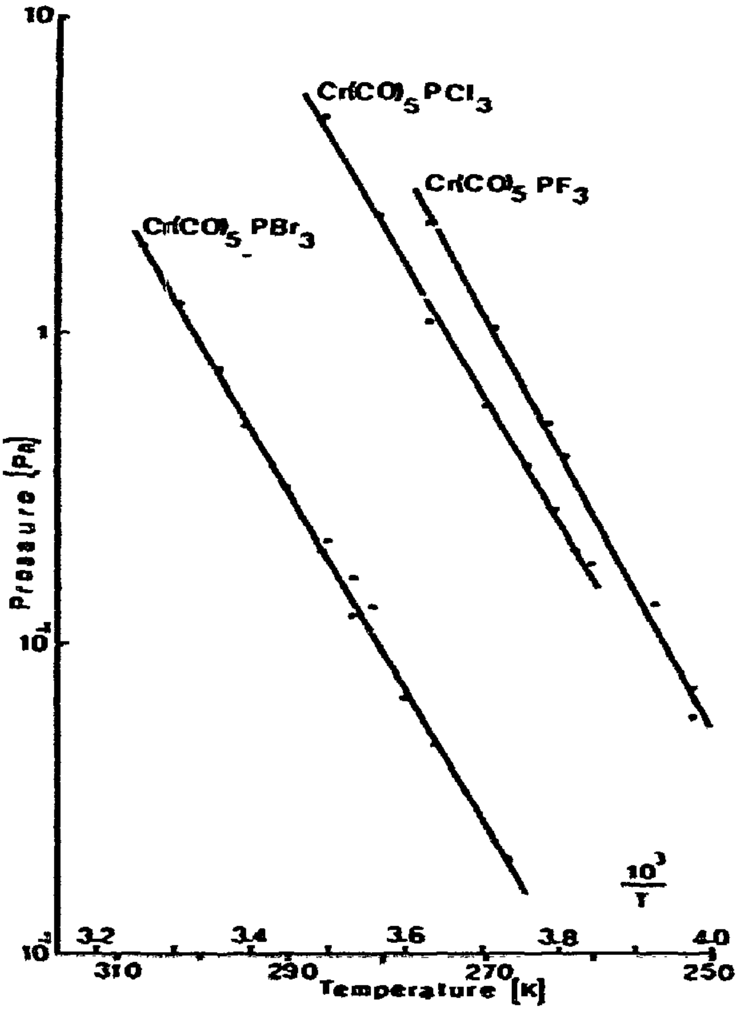

Fig. 2. Vapour pressures of the complexes $Cr(CO)_5PF_3$; $Cr(CO)_5PCl_3$; $Cr(CO)_5PBr_3$. A higher rate of weight loss during the first hours of measurements was observed for the $M(CO)_5PF_3$ complexes, probably due to a solvent impurity.

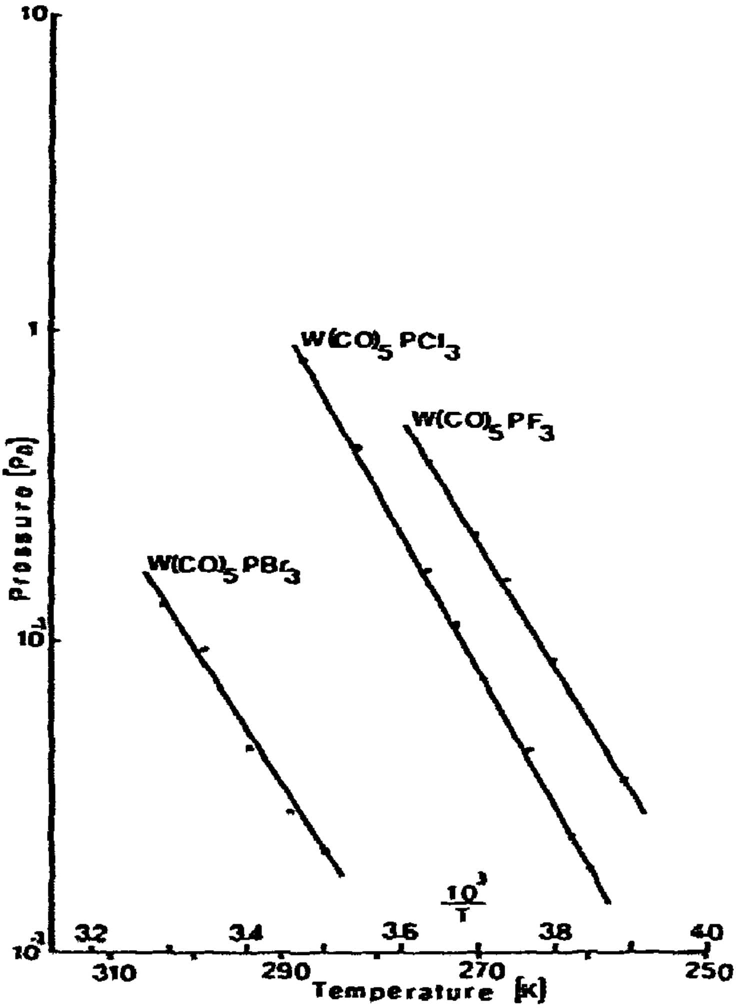

Fig. 3. Vapour pressures of the complexes $W(CO)_5PF_3$; $W(CO)_5PCl_3$; $W(CO)_5PBr_3$. A higher rate of weight loss during the first hours of the measurements was observed for the $M(CO)_5PF_3$ complexes, probably due to a solvent impurity.

TABLE 2

VAPOUR PRESSURES AND ENTHALPIES OF SUBLIMATION OF $M(CO)_5PX_3$

Sample	*Temp. (K)*	*Weight loss (kg sec^{-1}) (× 10^{-12})*	*Pressure (Pa) (× 10^{-1})*	$\ln p = -\frac{A}{T} + B$	*ΔH$_s$ (kJ mole^{-1})*
$Cr(CO)_5PF_3$^{a}	251.8	25	0.7	$A = 10300 \pm 300$	$\Delta H_s = 85.5 \pm 2.9$
	251.9	20	0.6	$B = 38.2$	
$M = 280.026^c$	255.0	47	1.4		
	263.0	140	4.2		
	264.7	173	5.2		
	269.7	359	10.9		
	275.7	753	23.1		
$Cr(CO)_5PCl_3$^{a}	260.8	66	1.8	$A = 9500 \pm 200$	$\Delta H_s = 78.9 \pm 1.8$
	261.9	74	2.0	$B = 34.6$	
$M = 329.385$	263.9	99	2.7		
	266.3	136	3.8		
	270.5	212	5.9		
	275.9	395	11.2		
	280.9	846	24.1		
	286.5	1701	49.0		
$Cr(CO)_5PBr_3$^{a}	268.0	9	0.2	$A = 9600 \pm 200$	$\Delta H_s = 79.9 \pm 1.9$
	275.1	20	0.5	$B = 32.0$	
$M = 462.753$	278.1	29	0.7		
	281.1	56	1.4		
	283.1	69	1.7		
	283.3	51	1.2		
	286.1	90	2.2		
	286.7	84	2.0		
	290.7	134	3.3		
	294.9	205	5.1		
	298.1	321	8.0		
	302.7	495	12.4		
	307.0	779	19.6		
$Mo(CO)_5PCl_3$^{a}	260.5	32	0.8	$A = 9540 \pm 130$	$\Delta H_s = 79.3 \pm 1.1$
	262.2	43	1.1	$B = 34.2$	
$M = 373.325$	264.7	67	1.7		
	267.3	87	2.3		
	269.2	115	3.0		
	272.2	159	4.2		
	272.5	165	4.4		
	275.1	221	5.9		
	278.1	335	8.9		
	280.6	444	11.9		
	281.3	509	13.6		
	287.1	975	26.4		
$W(CO)_5PF_3$^{a}	257.1	15	0.4	$A = 9310 \pm 180$	$\Delta H_s = 77.4 \pm 1.5$
	263.4	36	0.9	$B = 32.9$	
$M = 411.876$	267.7	65	1.6		
	270.7	90	2.3		
	275.1	152	3.8		

TABLE 2 *(continued)*

Sample	*Temp. (K)*	*Weight loss (kg sec⁻¹) (× 10⁻¹²)*	*Pressure (Pa) (× 10⁻¹)*	$\ln p = -\frac{A}{T} + B$	ΔH_s *(kJ mole⁻¹)*
$W(CO)_5PCl_3$[b]	260.1	47	0.2	$A = 10400 \pm 200$	$\Delta H_s = 86.2 \pm 1.7$
	261.9	61	0.2	$B = 35.8$	
M[c] $= 461.235$	265.7	92	0.4		
	270.0	196	0.8		
	272.5	291	1.2		
	275.3	429	1.7		
	282.3	1059	4.3		
	288.1	1988	8.1		
$W(CO)_5PBr_3$[a]	285.7	10	0.2	$A = 9290 \pm 640$	$\Delta H_s = 77.2 \pm 5.3$
	289.4	13	0.3	$B = 28.6$	
$M = 594.603$	294.0	22	0.5		
	298.7	43	0.9		
	303.7	60	1.3		

[a] Orifice diameter 0.1 mm.
[b] Orifice diameter 1 mm.
[c] Molecular weights in g.

TABLE 3

ENTHALPIES OF SUBLIMATION OF $M(CO)_6$ (KJ MOLE⁻¹)

$M(CO)_6$	*Connor et al.*[12a]	*Pilcher et al.*[12b]
$Cr(CO)_6$	71.2	71.8
$Mo(CO)_6$	70.8	73.8
$W(CO)_6$	81.2	76.5

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