Thermochimica Acta, 42 (1980) 343—348
Elsevier Scientific Publishing Company, Amsterdam — Printed in Belgium

SUBLIMATION ENTHALPIES OF THE COMPLEXES $W(CO)_{6-x}(NCCH_3)_x$ (x = 1, 2, 3) AND $Mo(CO)_{6-x}(NCCH_3)_x$ (x = 1, 3)

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(Received 13 June 1980)

ABSTRACT

Vapour pressure measurements have been carried out on the complexes $W(CO)_{6-x}(NCCH_3)_x$ (x = 1, 2, 3) and $Mo(CO)_{6-x}(NCCH_3)_x$ (x = 1, 3) employing the Knudsen effusion technique. The following enthalpies of sublimation, ΔH^{298}_{sub} (kJ mole^{-1}), have been determined from the vapour pressure data: $W(CO)_5(NCCH_3)$ = 98.1 ± 2.0; $W(CO)_4(NCCH_3)_2$ = 131.0 ± 6.0; $W(CO)_3(NCCH_3)_3$ = 103.4 ± 6.0; $Mo(CO)_5(NCCH_3)$ = 105.8 ± 5.6; and $Mo(CO)_3(NCCH_3)_3$ = 111.3 ± 3.0.

INTRODUCTION

Part of the research carried out in this department has been concerned with the thermochemistry and, in particular, the determination of enthalpies of sublimation, ΔH^{298}_{sub}, of the complexes $M(CO)_{6-x}L_x$ (M=Cr, Mo, W and L=P or N donor ligand) [1—5]. Earlier work on the measurement of vapour pressure employed an automated apparatus based on the isoteniscope method [6]. It is known, however, that static, direct pressure measuring apparatus of this type can lead to substantial errors if volatile impurities are present during the operation and it is evident that earlier published values for the enthalpy of sublimation of the complexes $W(CO)_{6-x}(NCCH_3)_x$ are in error [1].

In this paper, a Knudsen effusion cell has been employed to measure the vapour pressure and hence redetermine the enthalpies of sublimation of the above tungsten complexes. The complexes $Mo(CO)_5(NCCH_3)$ and $Mo(CO)_3(NCCH_3)_3$ have also been studied for comparison.

EXPERIMENTAL

The complexes were prepared by previously reported methods, $W(CO)_5(NCCH_3)$ [7]; $W(CO)_4(NCCH_3)_2$ [1]; $W(CO)_3(NCCH_3)_3$ [8]; $Mo(CO)_5(NCCH_3)$ [7]; and $Mo(CO)_3(NCCH_3)_3$ [8]. All solvents and reac-

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tants were carefully dried and purified by known methods. The purity of the complexes was checked by microanalysis and by IR spectroscopy in the carbonyl stretching region.

In this work, a Knudsen effusion apparatus and technique based on that of Wiedemann [9] has been employed. A description of the apparatus, its calibration and mode of operation have been given previously [10]. The Knudsen cell orifice diameters employed were 0.1 and 3.0 mm. The vacuum obtained during operation was better than 10^{-6} mm Hg and the temperature of each measurement was maintained constant to ±0.1 K. The accuracy in the rate of weight loss, $\Delta m/\Delta t$, was approximately 10^{-9} g sec^{-1}. The vapour pressure at each temperature was calculated employing the Knudsen equation

$$p = \left(\frac{\Delta m}{\Delta t}\right) \cdot \frac{1}{q} \sqrt{\frac{2\pi RT}{M}}$$

where p is the vapour pressure, q the calibrated orifice area, R the gas constant, T the absolute temperature and M the molecular weight of the sample vapour (in this work assumed to be the same as the crystalline sample). Plots of $\log_{10}p$ versus $1/T$ for each complex yielded straight lines described by the general equation

$$\log_{10}p = A - \frac{B}{T}$$

and the enthalpy of sublimation for each complex was calculated from the slope of the line, B. A least squares analysis of each set of data afforded a standard deviation for the ΔH^{298}_{sub} values.

Final purification of the complexes, i.e. removal of volatile impurities, including traces of $M(CO)_6$, which was present in several cases, was achieved by placing the complexes in the Knudsen cell and evacuating at 298 K and 10^{-6} mm Hg until the rate of weight loss was constant (usually overnight). A check on the progress of an experiment was maintained by randomly fluctuating the temperature of measurement for consecutive measurements.

RESULTS AND DISCUSSION

All complexes studied are thermally unstable and, consequently, experiments were carried out over the lowest possible temperature ranges. The complexes $M(CO)_3(NCCH_3)_3$ are extremely air sensitive; both complexes were found to be pyrophoric in air on removal from the Knudsen cell.

The measured vapour pressures and the enthalpies of sublimation for the five complexes are listed in Table 1. $\log_{10}P$ versus $1/T$ plots for the complexes are shown in Figs. 1 and 2.

No definitive trends in ΔH^{298}_{sub} values are observable when the metal centre is changed or with progressive substitution of CO by $NCCH_3$ for a given metal. Experimental error has masked any possible trend that may have been anticipated. The ΔH^{298}_{sub} values obtained for the complexes $Mo(CO)_5(NCCH_3)$ and $W(CO)_5$ $(NCCH_3)$ are consistent with values obtained for other pentacar-

TABLE 1

Vapour pressures and enthalpies of sublimation of $W(CO)_{6-x}(NCCH_3)_x$ (x = 1,2,3)

Complex	Temp. (K)	Weight loss (g sec^{-1}) × 10^9	Pressure (Nm^{-2})	$\log_{10}P = A - \frac{B}{T}$	ΔH_{sub}^{298} (kJ mole^{-1})
$W(CO)_5(NCCH_3)$	271.1	3.761	2.89×10^{-4}	A = 15.37	98.1 ± 2.0
	273.5	7.222	5.58×10^{-4}	B = 5129	
	275.8	6.667	5.17×10^{-4}		
	276.3	6.975	5.42×10^{-4}		
	278.1	12.071	9.41×10^{-4}		
	280.3	13.333	1.04×10^{-3}		
	283.8	25.278	1.99×10^{-3}		
	284.0	25.313	1.99×10^{-3}		
	285.8	37.500	2.96×10^{-3}		
	286.8	39.035	3.09×10^{-3}		
	287.2	33.333	2.64×10^{-3}		
	287.7	40.833	3.24×10^{-3}		
	289.2	57.778	4.59×10^{-3}		
	289.7	61.667	4.91×10^{-3}		
	290.5	69.000	5.50×10^{-3}		
	291.7	70.667	5.64×10^{-3}		
	293.7	105.278	8.43×10^{-3}		
	299.2	209.000	1.69×10^{-2}		
	302.0	311.875	2.53×10^{-2}		
	303.4	372.292	3.03×10^{-2}		
$W(CO)_4(NCCH_3)_2$	293.7	12.121	1.08×10^{-3}	A = 20.346	131.0 ± 6.0
	295.7	11.926	1.06×10^{-3}	B = 6852	
	296.2	17.302	1.55×10^{-3}		
	296.5	18.069	1.61×10^{-3}		
	298.1	27.778	2.49×10^{-3}		
	299.4	42.083	3.78×10^{-3}		
	300.2	35.690	3.21×10^{-3}		
	302.7	58.333	5.27×10^{-3}		
	302.9	75.833	6.85×10^{-3}		
	306.9	101.000	9.18×10^{-3}		
	307.7	139.444	1.27×10^{-2}		
	310.0	175.556	1.60×10^{-2}		
	313.0	288.269	2.65×10^{-2}		
$W(CO)_3(NCCH_3)_3$	307.6	29.167	7.99×10^{-2}	A = 16.399	103.4 ± 6.0
	307.9	26.905	7.37×10^{-2}	B = 5407	
	312.0	36.754	1.01×10^{-1}		
	318.1	69.804	1.94×10^{-1}		
	322.7	180.000	5.05×10^{-1}		
	322.7	136.667	3.83×10^{-1}		
	327.5	285.926	8.08×10^{-1}		
	332.9	566.667	1.61		
$Mo(CO)_5(NCCH_3)$	259.9	13.889	1.20×10^{-3}	A = 18.360	105.8 ± 5.6
	265.9	38.793	3.39×10^{-3}	B = 5533	
	265.9	45.960	4.02×10^{-3}		
	270.3	74.000	6.53×10^{-3}		
	271.6	122.222	1.08×10^{-2}		
	275.2	170.588	1.52×10^{-2}		
	279.2	447.619	4.01×10^{-2}		

TABLE 1 (continued)

Complex	Temp. (K)	Weight loss (g sec^{-1}) × 10^9	Pressure (Nm^{-2})	$\log_{10}P = A - \frac{B}{T}$	ΔH_{sub}^{298} (kJ mole^{-1})
$Mo(CO)_3(NCCH_3)_3$	283.2	15.476	1.34×10^{-3}	$A = 17.629$	111.3 ± 3.0
	283.7	16.912	1.46×10^{-3}	$B = 5821$	
	286.3	22.708	1.97×10^{-3}		
	290.7	39.333	3.44×10^{-3}		
	293.5	60.125	5.28×10^{-3}		
	297.5	115.625	1.02×10^{-2}		
	300.2	188.333	1.67×10^{-2}		
	304.4	440.417	3.94×10^{-2}		
	307.6	593.750	5.34×10^{-2}		

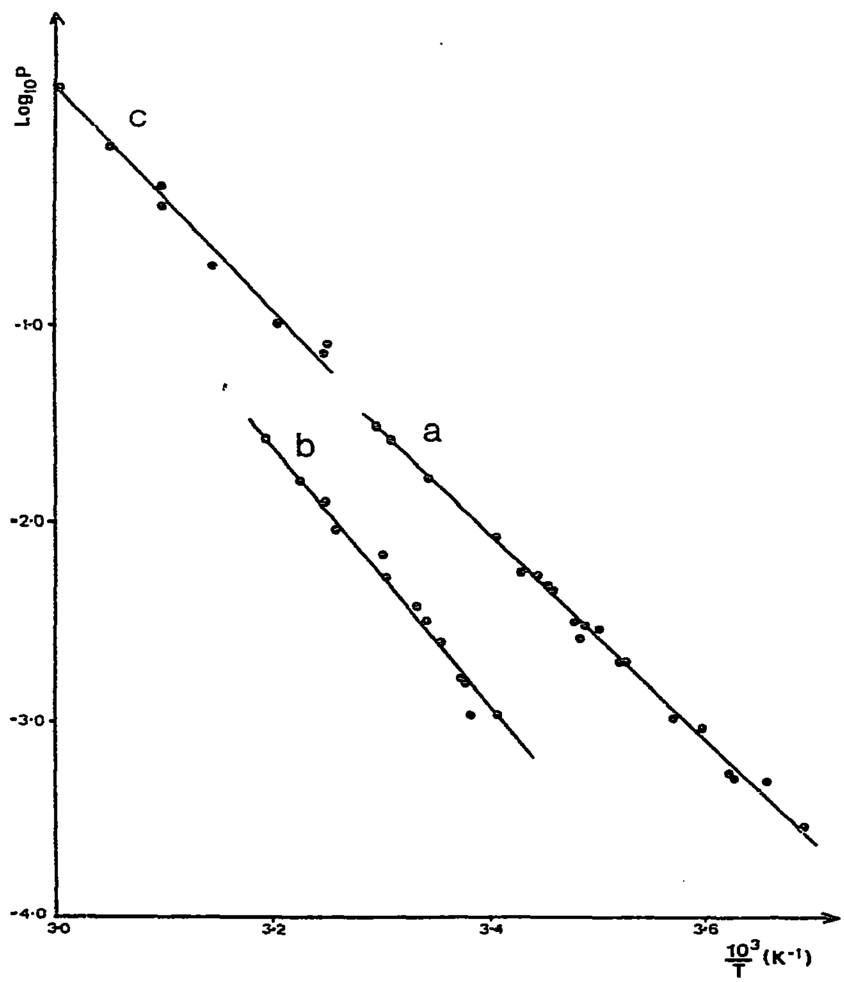

Fig. 1. $\log_{10}P$ versus $1/T$ plots for the complexes (a) $W(CO)_5(NCCH_3)$; (b) $W(CO)_4(NCCH_3)_2$; (c) $W(CO)_3(NCCH_3)_3$.

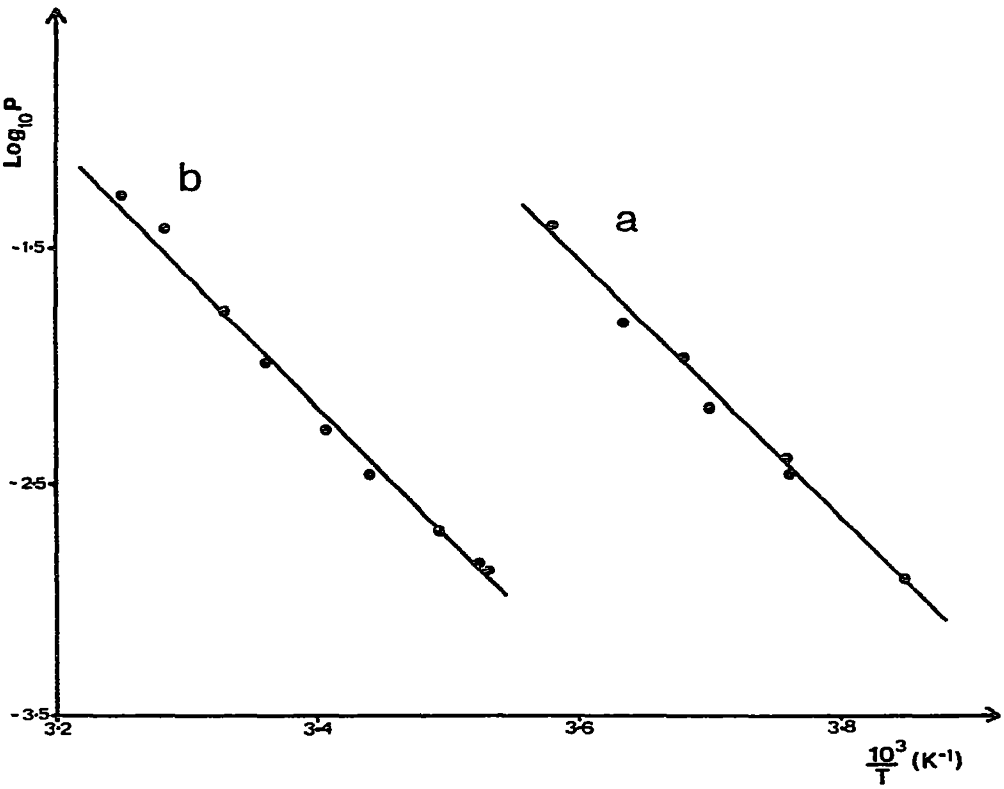

Fig. 2. $\log_{10}P$ versus $1/T$ plots for the complexes (a) $Mo(CO)_5(NCCH_3)$; (b) $Mo(CO)_3(NCCH_3)_3$.

bonyl complexes of Mo and W containing neutral N-donor ligands [2,11] (see Table 2). There is reasonable agreement between the measured ΔH^{298}_{sub} values obtained in this work for the complexes $Mo(CO)_3(NCCH_3)_3$ and $W(CO)_3(NCCH_3)_3$ and the values estimated by Skinner et al. [12] (96 and 100 kJ mole^{-1}, respectively).

ΔH^{298}_{sub} for $W(CO)_4(NCCH_3)_2$ appears to be surprisingly large and is pos-

TABLE 2

Comparison of ΔH^{298}_{sub} values for $M(CO)_5N$ (where M = Mo, W and N = neutral N-donor ligand)

Complex	ΔH^{298}_{sub}	Ref.
$Mo(CO)_5$piperidine	94.5 ± 2.9	2
$Mo(CO)_5$pyridine	102.0 ± 2.0	2
$Mo(CO)_5(NCCH_3)$	105.8 ± 5.6	This work
$W(CO)_5(NMe_3)$	89.1 ± 2.1	11
$W(CO)_5(NCCH_3)$	98.1 ± 2.0	This work
$W(CO)_5$piperidine	106.4 ± 1.0	2
$W(CO)_5$pyridazine	106.4 ± 2.5	11
$W(CO)_5$pyrazine	108.4 ± 1.3	2
$W(CO)_5$pyridine	109.7 ± 2.7	2
$W(CO)_5$pyrazole	112.5 ± 2.4	2

sibly due to the high thermal instability of this complex, which is known to disproportionate readily yielding the mono and tris acetonitrile complexes and which, like other numbers of this group, yields $M(CO)_6$, CO, and $NCCH_3$ on thermal decomposition.

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