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VAPOUR PRESSURE MEASUREMENTS ON (acac)M(SUBSTITUTED OLEFIN)$_2$ AND (acac)M(CO)$_2$ (M = Rh(I), Ir(I))

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ABSTRACT

Vapour pressures and enthalpies of sublimation of the complexes (acac)M (olefin)$_2$ and (acac)M(CO)$_2$ (M = Rh(I), Ir(I); olefin = ethylene, propylene, vinyl chloride, vinyl acetate and methyl acrylate) were determined by the Knudsen effusion method.

INTRODUCTION

Although numerous transition metal olefin complexes have been prepared and characterized, little is known about the vapour pressures and heats of sublimation of these complexes. This is primarily due to either the low thermal stability of these compounds or to a very low and almost undetectable vapour pressure. For compounds with a low vapour pressure the use of a Knudsen effusion cell is very suitable[1, 2].

In this laboratory, work is being carried out to obtain thermochemical data for the metal–ligand bond[3–5]. As part of this work, enthalpies of sublimation are used for the calculation of reaction enthalpies in the gas phase.

In this paper we report the vapour pressures and enthalpies of sublimation of complexes of the type (acac)M(CH$_2$=CHX)$_2$ (acac = acetyl acetonate; M = Rh(I), Ir(I); CH$_2$=CHX = ethylene (ET), propylene (PR), vinyl chloride (VCl), vinyl acetate (VA) and methyl acrylate (MA)), and also of the complexes (acac)Rh(CO)$_2$ and (acac)Ir(CO)$_2$.

EXPERIMENTAL

Preparation of the complexes

(acac)Rh(ET)$_2$ and (acac)Ir(ET)$_2$ were prepared according to literature methods[6, 7]. The other complexes were obtained by displacement of ET in the complexes (acac)Rh(ET)$_2$ or (acac)Ir(ET)$_2$ by an excess of olefin or CO. A detailed

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description of the synthesis and characterisation of these complexes has been presented in a previous paper (cf ref. 8). Benzoic acid was supplied by Mettler (melting point standard), and anthracene (p.a.) was supplied by Merck.

Thermochemical measurements

Measurements were made using a Mettler Thermoanalyser type 1. A Knudsen cell was placed on the balance as described by Wiedemann[1]. The vacuum was better than 2×10^{-6} mm Hg. The furnace consisted of an open Dewar flask[1] filled with water or ethanol in which a heating/cooling spiral and a stirrer were placed. The temperature was kept constant to $\pm$ 0.1 K. The cold trap was filled with liquid nitrogen. The construction of the Knudsen cell has been described by Wiedemann[1]. However, a modified orifice was used, which was made of 0.05 mm-thick Ni foil. The hole diameters were 1 and 3 mm. The sample weights were usually about 100 mg. The accuracy in $\Delta m/\Delta t$ was about 1×10^{-9} g sec^{-1}.

CALCULATIONS

Equilibrium vapour pressures were calculated according to 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, and M = molecular weight.

For each set of data a curve was fitted according to eqn. (2)

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

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

RESULTS AND DISCUSSION

The orifice area, which is dependent on the geometrical area and a form factor, was calibrated by measurements using anthracene and benzoic acid. Data from two different sources[1, 9] were used, and the results are given in Table 1.

It can be seen from Table 1 that the data of Wiedemann give the best corresponding orifice areas between anthracene and benzoic acid. For this reason, and because the data of Wiedemann were determined over nearly the same temperature range as ours, the orifice area was calibrated using only these data.

Because many organometallic compounds are thermally unstable it is necessary to investigate the existence of the complexes in the gas phase, and to determine whether or not decomposition occurs during the measurements.

TABLE 1

ORIFICE CALIBRATION OF THE KNUDSEN CELL

Sample	*Temperature (K)*	*Weight loss ($g\ sec^{-1}$)*	*Calc. from data of Wiedemann*[1]		*Calc. from data of Malaspina et al.*[9]	
			Pressure (mm Hg)	*Orifice area (cm^2)*	*Pressure (mm Hg)*	*Orifice area (cm^2)*
Anthracene[a]	323.7	49×10^{-9}	2.73×10^{-4}	41.7×10^{-4}	2.06×10^{-4}	55.0×10^{-4}
M = 178.24	326.7	64×10^{-9}	3.64×10^{-4}	40.6×10^{-4}	2.91×10^{-4}	51.1×10^{-4}
	332.4	120×10^{-9}	6.19×10^{-4}	45.3×10^{-4}	5.50×10^{-4}	51.1×10^{-4}
	338.5	216×10^{-9}	10.72×10^{-4}	47.6×10^{-4}	10.63×10^{-4}	48.0×10^{-4}
Benzoic acid[a]	292.9	110×10^{-9}	6.72×10^{-4}	43.6×10^{-4}	6.43×10^{-4}	45.4×10^{-4}
M = 122.12	295.7	158×10^{-9}	9.42×10^{-4}	44.7×10^{-4}	8.98×10^{-4}	45.8×10^{-4}
	298.9	223×10^{-9}	13.74×10^{-4}	43.6×10^{-4}	13.08×10^{-4}	45.7×10^{-4}
	301.5	325×10^{-9}	18.57×10^{-4}	47.1×10^{-4}	17.63×10^{-4}	49.7×10^{-4}
	305.3	462×10^{-9}	28.56×10^{-4}	43.9×10^{-4}	27.05×10^{-4}	46.3×10^{-4}
	Orifice diameter 1 mm; mean value for q[b]: $(4.4 \pm 0.2)\ 10^{-3}\ cm^2$.					
Anthracene[c]	297.5	19×10^{-9}	1.74×10^{-5}	2.39×10^{-2}	0.76×10^{-5}	5.57×10^{-2}
M = 178.24	302.2	31×10^{-9}	2.95×10^{-5}	2.33×10^{-2}	1.43×10^{-5}	4.85×10^{-2}
	306.5	50×10^{-9}	4.72×10^{-5}	2.37×10^{-2}	2.51×10^{-5}	4.49×10^{-2}
	310.1	81×10^{-9}	6.92×10^{-5}	2.64×10^{-2}	3.97×10^{-5}	4.61×10^{-2}
	313.1	118×10^{-9}	9.47×10^{-5}	2.84×10^{-2}	5.78×10^{-5}	4.64×10^{-2}
	319.6	226×10^{-9}	18.28×10^{-5}	2.84×10^{-2}	12.73×10^{-5}	4.88×10^{-2}
	Orifice diameter 3 mm; mean value for q[b]: $(2.6 \pm 0.2).10^{-2}\ cm^2$.					

[a] Orifice diameter 1 mm.

[b] Only data from Wiedemann[1] were used, see text.

[c] Orifice diameter 3 mm.

The complexes (acac)M$(CO)_2$, (acac)M$(ET)_2$ and (acac)M$(PR)_2$ (M = Rh, Ir) can be sublimed, and good mass spectra (A.E.I. MS9, 70 eV) were obtained from (acac)Rh$(ET)_2$, (acac)Rh$(VA)_2$, and (acac)Rh$(MA)_2$, and also from (acac)Rh$(CO)_2$ and (acac)Ir$(CO)_2$[10]. It was therefore assumed that all complexes do exist in the gas phase.

In order to investigate if decomposition occurs during the measurements, elemental analyses of all complexes were made before and after each vapour pressure measurement. Decomposition of the complex would certainly increase the percentage of metal in the sample, but it can be seen from Table 2 that no significant decomposition occurred during the measurements.

The measured vapour pressures and enthalpies of sublimation of the complexes are presented in Table 2 and are shown graphically in Fig. 1.

Some samples gave a higher rate of weight loss during the first 24 hours, which was probably due to the presence of residual solvent or free ligand molecules in the sample. (The accuracy of the elemental analysis, ± 0.3%, was not sufficient to detect the latter effect.)

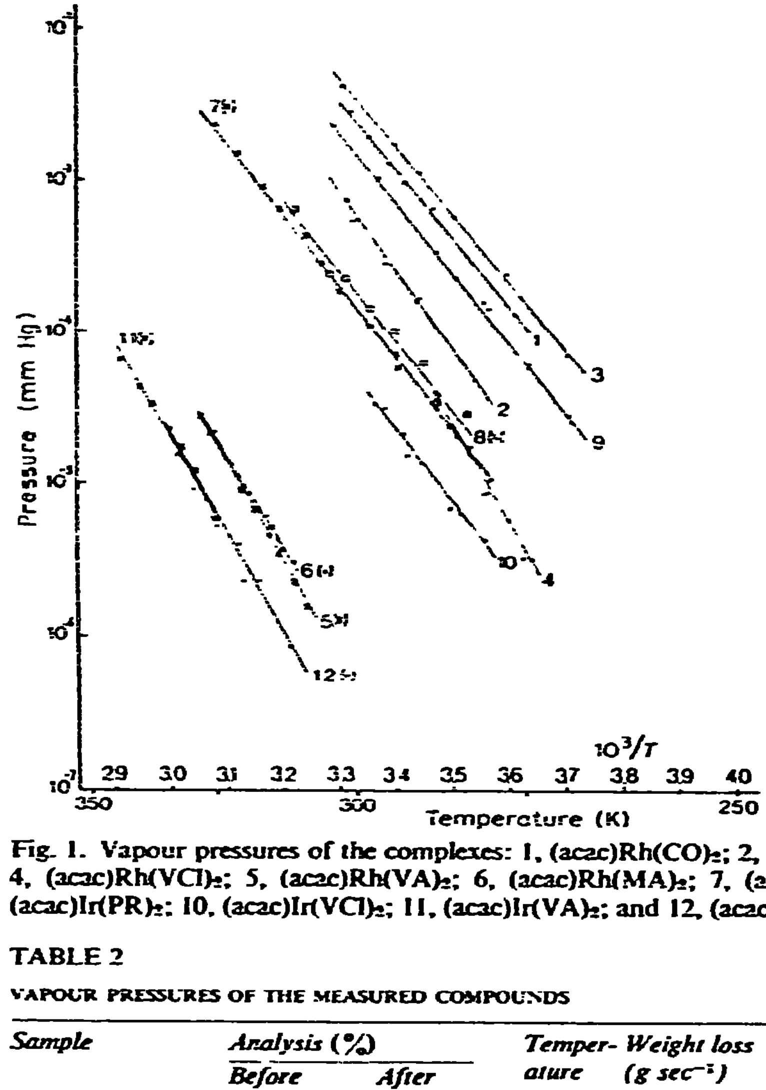

Fig. 1. Vapour pressures of the complexes: 1, (acac)Rh(CO)$_2$; 2, (acac)Rh(ET)$_2$; 3, (acac)Rh(PR)$_2$; 4, (acac)Rh(VCl)$_2$; 5, (acac)Rh(VA)$_2$; 6, (acac)Rh(MA)$_2$; 7, (acac)Ir(CO)$_2$; 8, (acac)Ir(ET)$_2$; 9, (acac)Ir(PR)$_2$; 10, (acac)Ir(VCl)$_2$; 11, (acac)Ir(VA)$_2$; and 12, (acac)Ir(MA)$_2$.

TABLE 2

VAPOUR PRESSURES OF THE MEASURED COMPOUNDS

Sample	*Analysis (%)*		*Temperature (K)*	*Weight loss (g sec^{-1})*	*Pressure (torr)*	$\log p = B - \frac{A}{T}$
	Before Knudsen measurement	*After Knudsen measurement*				
(acac)Rh(CO)$_2$^{a}	C: 32.45	C: 32.46	276.3	30×10^{-9}	1.2×10^{-4}	
$M = 258.035$	H: 2.69	H: 2.74	288.5	152×10^{-9}	6.2×10^{-4}	
	O: 24.79	O: 24.77	292.7	223×10^{-9}	9.2×10^{-4}	$A = 4500 \pm 150$
			295.5	302×10^{-9}	12.5×10^{-4}	$B = 12.4$
			298.3	455×10^{-9}	19.0×10^{-4}	
			300.9	682×10^{-9}	28.5×10^{-4}	$\Delta H_s = 20.6 \pm 0.7$ kcal mol^{-1}
(acac)Rh(ET)$_2$^{a}	C: 41.82	C: 42.10	282.5	11×10^{-9}	0.5×10^{-4}	
$M = 258.122$	H: 5.90	H: 5.95	290.7	38×10^{-9}	1.6×10^{-4}	
	O: 12.32	O: 12.90	291.1	37×10^{-9}	1.5×10^{-4}	$A = 5124 \pm 186$
			295.9	67×10^{-9}	2.8×10^{-4}	$B = 13.8$
			300.1	127×10^{-9}	5.3×10^{-4}	
			300.9	126×10^{-9}	5.3×10^{-4}	$\Delta H_s = 23.4 \pm 0.9$ kcal mol^{-1}
			301.5	169×10^{-9}	7.1×10^{-4}	

TABLE 2 *(continued)*

Sample	*Analysis (%)*		*Temperature (K)*	*Weight loss (g sec^{-1})*	*Pressure (torr)*	*$\log p = B - \frac{A}{T}$*
	Before Knudsen measurement	*After Knudsen measurement*				
(acac)Rh(PR)$_2$[a]	C: 45.89	C: 45.85	270.1	18×10^{-9}	0.7×10^{-4}	
M = 286.176	H: 6.75	H: 6.78	278.1	61×10^{-9}	2.3×10^{-4}	$A = 4507 \pm 85$
	O: 11.69	O: 11.73	283.5	118×10^{-9}	4.6×10^{-4}	$B = 12.5$
			285.3	143×10^{-9}	5.5×10^{-4}	
			290.5	277×10^{-9}	10.8×10^{-4}	$\Delta H_s = 20.6 \pm 0.4$
			294.0	429×10^{-9}	16.8×10^{-4}	kcal mol^{-1}
			302.5	1032×10^{-9}	41.1×10^{-4}	
(acac)Rh(VCl)$_2$[b]	C: 33.32	C: 33.12	274.9	5×10^{-9}	3.2×10^{-6}	
M = 327.012	H: 4.20	H: 4.04	275.9	5×10^{-9}	3.2×10^{-6}	$A = 6125 \pm 375$
	O: 9.67	O: 10.05	278.1	9×10^{-9}	5.8×10^{-6}	$B = 16.8$
	Cl: 21.36	Cl: 21.63	280.6	16×10^{-9}	10.0×10^{-6}	
			281.0	14×10^{-9}	8.5×10^{-6}	$\Delta H_s = 28.0 \pm 1.7$
			281.3	14×10^{-9}	8.5×10^{-6}	kcal mol^{-1}
			281.3	19×10^{-9}	11.8×10^{-6}	
			283.3	27×10^{-9}	16.7×10^{-6}	
			285.5	31×10^{-9}	19.6×10^{-6}	
			288.1	48×10^{-9}	29.9×10^{-6}	
(acac)Rh(VA)$_2$[b]	C: 41.73	C: 41.65	308.5	3×10^{-9}	1.6×10^{-6}	
M = 374.196	H: 5.15	H: 5.11	310.6	4×10^{-9}	2.2×10^{-6}	$A = 6340 \pm 172$
	O: 25.39	O: 25.51	313.4	6×10^{-9}	3.5×10^{-6}	$B = 14.8$
			315.1	8×10^{-9}	5.0×10^{-6}	
			317.7	11×10^{-9}	6.8×10^{-6}	$\Delta H_s = 29.0 \pm 0.8$
			320.4	14×10^{-9}	8.9×10^{-6}	kcal mol^{-1}
			327.9	44×10^{-9}	27.6×10^{-6}	
(acac)Rh(MA)$_2$[b]	C: 41.70	C: 41.03	310.7	5×10^{-9}	3.0×10^{-6}	
M = 374.196	H: 5.20	H: 5.15	313.1	6×10^{-9}	3.7×10^{-6}	$A = 5839 \pm 247$
	O: 25.60	O: 25.63	313.1	6×10^{-9}	3.4×10^{-6}	$B = 13.2$
			314.8	7×10^{-9}	4.4×10^{-6}	
			316.0	10×10^{-9}	6.0×10^{-6}	$\Delta H_s = 26.7 \pm 1.1$
			318.9	14×10^{-9}	8.6×10^{-6}	kcal mol^{-1}
			325.5	34×10^{-9}	21.4×10^{-6}	
			326.5	33×10^{-9}	20.6×10^{-6}	
(acac)Ir(CO)$_2$[a]	C: 24.04	C: 24.14	286.2	7×10^{-9}	0.2×10^{-4}	
M = 347.330	H: 2.08	H: 2.11	294.0	16×10^{-9}	0.6×10^{-4}	$A = 4821 \pm 68$
	O: 18.48	O: 18.47	294.2	19×10^{-9}	0.7×10^{-4}	$B = 12.2$
			298.1	29×10^{-9}	1.0×10^{-4}	
			303.0	49×10^{-9}	1.8×10^{-4}	$\Delta H_s = 22.0 \pm 0.3$
			306.0	76×10^{-9}	2.8×10^{-4}	kcal mol^{-1}
			308.7	114×10^{-9}	4.2×10^{-4}	
			313.1	166×10^{-9}	6.1×10^{-4}	
			316.0	233×10^{-9}	8.6×10^{-4}	
			320.6	390×10^{-9}	14.5×10^{-4}	
			325.1	599×10^{-9}	22.5×10^{-4}	

TABLE 2 *(continued)*

Sample	*Analysis (%)*		*Temperature (K)*	*Weight loss (g sec^{-1})*	*Pressure (torr)*	*log p = B − $\frac{A}{T}$*
	Before Knudsen measurement	*After Knudsen measurement*				
(acac)Ir(ET)$_2$^{a}	C: 31.17	C: 31.34	283.5	8×10^{-9}	0.3×10^{-4}	
M = 347.417	H: 4.37	H: 4.53	287.7	9×10^{-9}	0.3×10^{-4}	A = 4324 ± 238
	O: 9.38	O: 9.34	290.3	17×10^{-9}	0.6×10^{-4}	B = 10.6
			294.7	27×10^{-9}	0.9×10^{-4}	
			298.5	38×10^{-9}	1.4×10^{-4}	ΔH_s = 19.8 ± 1.0
			302.2	59×10^{-9}	2.1×10^{-4}	kcal mol^{-1}
			305.0	64×10^{-9}	2.3×10^{-4}	
			310.7	166×10^{-9}	6.1×10^{-4}	
(acac)Ir(PR)$_2$^{a}	C: 35.25	C: 35.56	269.7	7×10^{-9}	0.2×10^{-4}	
M = 375.47	H: 5.10	H: 5.12	270.0	8×10^{-9}	0.3×10^{-4}	A = 4697 ± 71
	O: —	O: 8.26	275.4	18×10^{-9}	0.6×10^{-4}	B = 12.8
			275.4	16×10^{-9}	0.5×10^{-4}	
			280.6	41×10^{-9}	1.4×10^{-4}	ΔH_s = 21.5 ± 0.3
			281.3	45×10^{-9}	1.5×10^{-4}	kcal mol^{-1}
			285.1	65×10^{-9}	2.2×10^{-4}	
			288.1	95×10^{-9}	3.2×10^{-4}	
			296.7	287×10^{-9}	9.9×10^{-4}	
			303.7	637×10^{-9}	22.2×10^{-4}	
(acac)Ir(VCl)$_2$^{b}	C: 25.80	C: 25.99	281.3	8×10^{-9}	4.3×10^{-6}	
M = 416.307	H: 3.24	H: 3.33	284.5	11×10^{-9}	6.3×10^{-6}	A = 4684 ± 225
	O: 7.82	O: 7.90	286.0	12×10^{-9}	6.8×10^{-6}	B = 11.3
	Cl: 16.53	Cl: 16.38	290.5	24×10^{-9}	13.1×10^{-6}	
			292.5	27×10^{-9}	15.2×10^{-6}	ΔH_s = 21.4 ± 1.0
			293.1	36×10^{-9}	20.4×10^{-6}	kcal mol^{-1}
			296.2	54×10^{-9}	30.4×10^{-6}	
			297.7	58×10^{-9}	32.6×10^{-6}	
(acac)Ir(VA)$_2$^{b}	C: 33.84	C: 33.85	325.1	11×10^{-9}	5.8×10^{-6}	
M = 463.491	H: 4.19	H: 4.36	329.1	21×10^{-9}	11.8×10^{-6}	A = 6284 ± 163
	O: 20.63	O: 20.67	331.7	28×10^{-9}	15.7×10^{-6}	B = 14.1
			332.9	32×10^{-9}	18.1×10^{-6}	
			337.2	57×10^{-9}	32.2×10^{-6}	ΔH_s = 28.8 ± 0.7
			339.6	72×10^{-9}	41.2×10^{-6}	kcal mol^{-1}
			343.5	118×10^{-9}	67.6×10^{-6}	
(acac)Ir(MA)$_2$^{b}	C: 33.87	C: 34.28	311.5	2×10^{-9}	0.8×10^{-6}	
M = 463.491	H: 4.20	H: 4.25	317.3	4×10^{-9}	2.3×10^{-6}	
	O: 20.70	O: 20.60	319.9	4×10^{-9}	2.3×10^{-6}	
			320.9	7×10^{-9}	4.0×10^{-5}	A = 6120 ± 268
			325.0	9×10^{-9}	5.2×10^{-6}	B = 13.6
			327.0	14×10^{-9}	7.8×10^{-6}	
			327.5	14×10^{-9}	7.8×10^{-6}	ΔH_s = 28.0 ± 1.2
			329.4	16×10^{-9}	9.2×10^{-6}	kcal mol^{-1}
			332.6	28×10^{-9}	15.6×10^{-6}	
			335.3	41×10^{-6}	23.5×10^{-6}	

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[a] Orifice diameter 1 mm.

[b] Orifice diameter 3 mm.

Attempts to determine the vapour pressures of the complexes (acac)Rh(styrene)$_2$ and (acac)Ir(styrene)$_2$ failed because the rate of weight loss was too low.

Table 2 and Fig. 1 show that the complexes under discussion have vapour pressures and heats of sublimation comparable, for example, with those of $Cr(C_6H_6)(CO)_3$[2].

The sublimation enthalpies of the VA and MA complexes are higher than those of the other complexes, probably because of the larger dipole moments of VA and MA (VA, $\mu_D = 1.7$; MA, estimated $\mu_D = 1.7$; CO, $\mu_D = 0.1$; ET, $\mu_D = 0$; PR, $\mu_D = 0.34$; and VCl, $\mu_D = 1.42$)[11]. The deviation in the values for the VCl complexes are more difficult to explain. (acac)Rh(VCl)$_2$ has a sublimation enthalpy that is in accord with the value expected on the basis of the dipole moment of VCl, but, on the other hand, the sublimation enthalpy of (acac)Ir(VCl)$_2$ is rather low.

The solid state structures of (acac)Rh(CO)$_2$ and (acac)Ir(CO)$_2$ are known[12]. Although these structures show a significant interaction between the metal atoms of neighbouring molecules, this interaction is not reflected in the enthalpy of sublimation.

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