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Thermal Stability, Sublimation Pressures, and Diffusion Coefficients of Anthracene, Pyrene, and Some Metal *β*-Diketonates

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Metal β-diketonates are often volatile enough to be useful as precursors of metals in vapor phase deposition processes, e.g., chemical vapor deposition (CVD). To engineer such processes, knowledge of vapor or sublimation pressures is essential because they determine the maximum theoretical growth rate and the composition. Gaseous diffusion coefficients are needed for calculation of Sherwood and Lewis numbers used to describe the mass transfer process. Such data are often either lacking or not well established. In the present communication, the thermal stabilities of copper(II) acetylacetonate, vanadium(III) acetylacetonate, zinc(II) acetylacetonate, ruthenium(III) acetylacetonate, thulium(III) acetylacetonate, and dysprosium(III) acetylacetonate are tested. Some of these compounds are sensitive to air (oxygen), and hence the studies have been performed in a glovebox to avoid any oxygen and moisture. The vapor pressures and the binary diffusion coefficients (in nitrogen or helium) for anthracene, pyrene, copper(II) acetylacetonate, and ruthenium(III) acetylacetonate are reported at temperatures between (339 and 443) K at ambient pressure. The enthalpies of sublimation are also deduced from the vapor pressure data. The discrepancies with literature data, found in some cases, are discussed.

1. Introduction

Species with low but observable vapor pressures are interesting for several applications. One of these is chemical vapor deposition (CVD). In this process, the precursor molecules (which often are organometallic compounds) are evaporated. In such a process, after the evaporation of one or more precursor molecules that include the elements which shall be present in a deposited thin film (or coating), they are mixed and attached to a substrate. There, energy (thermal energy) is provided to initiate a chemical reaction so that films of metals, oxides, or other compounds are formed. To engineer such a process knowledge of the vapor or sublimation pressures is essential because they determine the maximum theoretical growth rate and the composition. Due to the low vapor pressures and consequently the requirement of a sophisticated experimental procedure, often either no information is available or the data are contradictory. The latter may be because of different reasons: some of the precursors used are not thermally stable, so that evaporation may be accompanied by pyrolysis; some are sensitive to air; and sometimes the methods might not have been appropriate. Since thermal balances are available in many laboratories, it is evident that different researchers try to use these devices to measure the needed data.

We have started a program to study the long-term thermal stability, sublimation pressures, and diffusion coefficients of organometallic compounds. Recently, the thermal behavior of some selected metal acetylacetonates was reported.[1,2] The structure, vaporization, and thermal decomposition of a number of acetylacetonates at higher temperatures have been studied using a mass spectroscopic technique.[3−5] In the present communication, the evaporation behavior of some more, viz., copper(II) acetylacetonate [$\mathrm{Cu(acac)_2}$], vanadium(III) acetylacetonate [$\mathrm{V(acac)_3}$], zinc(II) acetylacetonate [$\mathrm{Zn(acac)_2}$], ruthenium(III) acetylacetonate [$\mathrm{Ru(acac)_3}$], thulium(III) acetylacetonate [$\mathrm{Tm(acac)_3}$], and dysprosium(III) acetylacetonate, [$\mathrm{Dy(acac)_3}$], are investigated. Some of these compounds are highly sensitive to air (oxygen and moisture). The reported sublimation pressure values for some of these (e.g., [$\mathrm{Cu(acac)_2}$]) are highly contradictory (the details follow in the section Results and Discussion). We have measured these substances with great care in the absence of oxygen and moisture. Apart from these two well-known compounds, anthracene and pyrene were also investigated as their diffusion coefficients (D_{AB}) are known only over a limited low temperature range. The diffusion coefficients are needed for the calculation of the Sherwood (Sh) and Lewis (Le) numbers used to describe mass transfer processes (e.g., to calculate the buffer gas saturation in evaporators).

$$\mathrm{Sh} = \frac{h_{\mathrm{M}}L}{D_{\mathrm{AB}}} \tag{1}$$

$$\mathrm{Le} = \frac{\alpha}{D_{\mathrm{AB}}} \tag{2}$$

where h_{M} is the convection mass transfer coefficient; L is a characteristic length; and α is the thermal conductivity.

The diffusion coefficient data for such substances are scarce in the literature, and no data are available for metal β-diketones. In our recent publications,[1,2] the diffusion coefficients of naphthalene, phenanthrene, ferrocene, tris(2,2,6,6-tetramethyl-3,5-heptanedianato)cobalt(III), aluminum(III) acetylacetonate, and chromium(III) acetylacetonates in nitrogen/air were reported. These were obtained by combining the thermogravimetric measurements and precise vapor pressures obtained from a Knudsen cell method. The main idea behind this method is that the evaporation out of a crucible is a nearly one-dimensional diffusion process, which depends on the vapor pressure and the

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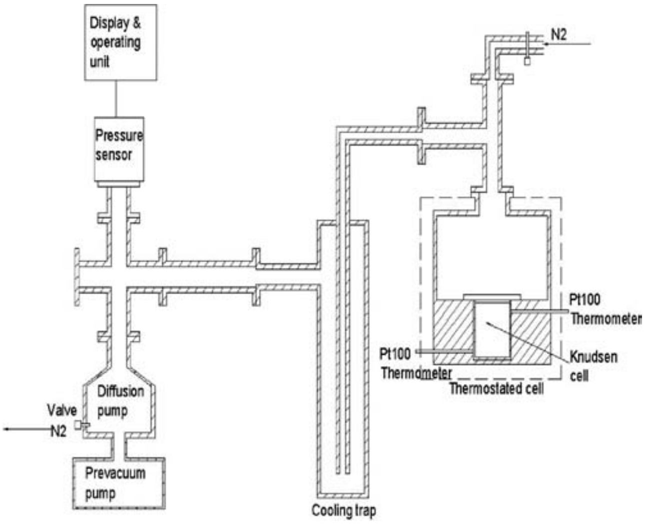

Figure 1. Experimental setup for measuring the vapor pressure.

diffusion coefficient; if either is known, the other can be obtained from thermogravimetric mass loss rates. The same method is used here.

2. Experimental Section

Anthracene (Alfa Aesar > 99.9 %) and pyrene (Alfa Aesar 99 %) were used without further purification. [Cu(acac)$_2$] (Sigma Aldrich, 99.99 %), [V(acac)$_3$] (Alfa Aesar, > 97 %), [Zn(acac)$_2$] (ABCR > 98 %), [Ru(acac)$_3$] (ABCR > 99 %), [Tm(acac)$_3$] (Alfa Aesar > 99 %), and [Dy(acac)$_3$] (Alfa Aesar > 99 %) were purchased. For the vapor pressure measurements, these were purified by sublimation. Some measurements were also performed using untreated samples. The vapor pressures of the purified samples did not differ from those of the untreated samples. Hence for further thermogravimetric experiments, the substances were used as received. N$_2$ (99.98 %) or He (99.998 %) were used as carrier gases.

Most of the metal β-diketonates were sensitive to moisture and/or oxygen and were handled appropriately. The substances were stored in a glovebox and filled into the Knudsen cell also in the glovebox. A home-built stainless steel Knudsen cell was used for vapor pressure measurements. The experimental setup has been described in a previous publication[1] and was modified slightly to make measurements under an inert gas atmosphere. A schematic diagram is shown in Figure 1.

The setup includes a Knudsen cell, two Pt100 thermometers, a stainless steel thermostatted vessel (vacuum chamber), a cooling trap, a diffusion pump, a prevacuum pump, a pressure sensor with a display, and an operating unit and arrangement for flushing inert gas (e.g., nitrogen). The Knudsen cell is situated in a vacuum chamber, with good thermal contact around the cell. The temperature of the stainless steel chamber is controlled with a PID temperature controller. The heating was performed with an electrical band heater which was wrapped around the chamber carefully to cover it completely. The outer side was then covered with insulation material. The temperature was measured at two different places inside the chamber and did not differ more than 0.1 K. The difference between the actual evaporation temperature (inside the Knudsen cell) and the measured chamber temperature was determined in many experiments performed before the actual measurements by bringing a calibrated Pt-100 thermometer inside the Knudsen cell and measuring its temperature. This temperature difference which was different for different temperatures was always taken into account to correct the display temperature. It was ensured that the thermal equilibrium between the sample and the thermal reservoir (chamber) was attained. A provision for circulating the nitrogen gas was made to prevent the degradation of substances by atmospheric air and moisture before the evacuation. This was done by making an inlet at the top of the heating cell for introducing the nitrogen into the experimental setup and an outlet through a valve in the diffusion pump. In this way, the circulation of nitrogen was ensured during the heating period.

A well-defined amount of the substance (depending upon the temperature of the measurement and the substance) was weighed into the cell. The filling and weighing was done under an inert gas atmosphere in a glovebox. The cell was then tightened and put into the vacuum chamber. The thickness of the aluminum foil used was 70 μm. The temperature of the chamber was maintained constant to better than $\pm$ 0.2 K. Prior to evacuation, enough time (at least 60 min) was allowed for the attainment of a constant temperature which was recorded with the help of a calibrated Pt-100 thermometer. During this time, a nitrogen atmosphere was maintained in the chamber. It was ensured that the substance evaporated before evacuating the cell was less than the accuracy of the measurement. The evacuation of the chamber was then started, and the time interval was measured between the time when the vacuum reached a pressure of around 10^{-3} Pa and the time when the high vacuum pump was turned off and the pressure was above 10^{-3} Pa. Typical times were (1 to 20) h [in this time, the weight losses were between (4 and 50) mg depending on the hole size (ranging from (0.4 to 0.7) mm), the temperature, and the substance]. The cell was then brought to room temperature in a desiccator and weighed again. The system was regularly tested with reference substances[6] (ferrocene,[1] phenanthrene,[1] anthracene, and pyrene) having different vapor pressures to cover the range of the vapor pressures to be measured and proved to furnish reliable results over a large temperature range. More details are given in ref 1. The uncertainties in the evaporation time and in the mass loss are estimated to be 0.5 min and 0.05 mg, respectively. In the evaluation of the data, no additional calibration was performed. The maximum overall uncertainty in vapor pressure measurements was estimated to be ($\pm$ 0.1 to $\pm$ 0.5) Pa in the pressure range (10 to 50) Pa and ($\pm$ 0.02 to $\pm$ 0.1) Pa in the lower pressure range (0.02 to 10) Pa. This overall uncertainty was calculated assuming that the uncertainties in evaporation time, mass loss, and the correction factor are independent and random.

A commercial TGA/DTA (Bähr STA 503) was used to perform the thermogravimetric experiments. The apparatus as well as the microbalance was kept in a glovebox to avoid any contact of the sample with oxygen or water vapor. The carrier gas was N$_2$ or helium. The flow rate of 100 $\mathrm{cm^3 \cdot min^{-1}}$ (for nitrogen) was controlled by a calibrated mass flow controller. This flow rate was found to be sufficient to ensure that the concentration of substance at the top of the crucible remains nearly zero throughout the measurement as proved experimentally: a change in flow rate did not change the mass loss rate measurably. The pressure was atmospheric throughout. Open alumina crucibles were used in all experiments, the inner diameter being 5.35 mm and the inner height 7.2 mm. The samples were filled inside the crucible, so that the initial height of the sample inside the crucible was between (3.0 and 5.0) mm. From the initial height, which was measured at the beginning of each experiment with an estimated precision of $\pm$ 0.2 mm, the volume of the sample was calculated. Using the initial mass, the apparent density of the sample was derived. The temperature was typically reached within 30 min, and then

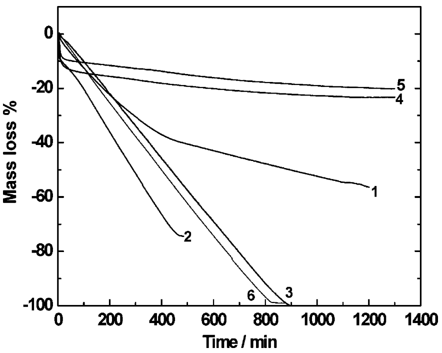

Figure 2. TGA curve in isothermal mode for some selected substances: 1, [V(acac)$_3$]; 2, [Zn(acac)$_2$]; 3, [Cu(acac)$_2$]; 4, [Dy(acac)$_3$]; 5, [Tm(acac)$_3$]; 6, [Ru(acac)$_3$].

the temperature was held constant, in some experiments, until all the sample was evaporated. In other experiments, the temperature was changed after 2 h to the next temperature so that several temperatures could be investigated within one run. The temperature sensor was calibrated by measuring the melting points of reference substances (4-nitrotoluene, naphthalene, indium, and potassium perchlorate) which cover the whole temperature range of the measurements. The uncertainty in mass loss rate was estimated to be ± 1 % and ± 10 % for the apparent density and for the diffusion coefficient (± 0.005 to ± 0.05) $\text{cm}^2\cdot\text{s}^{-1}$ depending on the system and arising mainly from the uncertainties in the initial distance between the sample surface and the top of the crucible. This overall uncertainty in diffusion coefficient was calculated considering the uncertainties in vapor pressure, initial height of the sample, and the mass loss rate given above to be independent and random.

3. Results and Discussion

The stability of the compounds was investigated by isothermal thermogravimetry (TGA). These experiments try to simulate typical evaporator conditions, which are held at constant temperatures. From theory, in an isothermal TGA a nearly linear mass loss as a function of time is expected, and no residual should remain. Some typical results from the TGA are summarized in Figure 2. [V(acac)$_3$] leaves 18 % residue in an isothermal evaporation at 194 °C. Hosono et al.[7] studied the thermal decomposition behavior of some zinc compounds and reported the decomposition of [Zn(acac)$_2$] below 200 °C. We also found that it leaves about 25 % residue on isothermal evaporation at 95 °C. [Tm(acac)$_3$] and [Dy(acac)$_3$] leave more than 80 % residue on isothermal evaporation at 117 °C. It was also observed in separate experiments that for these substances the decomposition accompanies the evaporation process, even at lower temperatures, and therefore no vapor pressure measurements were done using the Knudsen cell method, which, as a gravimetric method, relies on the intact evaporation of the studied compound.

On the other hand, [Cu(acac)$_2$] and [Ru(acac)$_3$] evaporate without residuals, and hence their sublimation pressures at various temperatures were measured at different temperatures together with the reference substances anthracene and pyrene.

The vapor pressures p were determined from the measurement of the mass of the substance Δm evaporated in a definite time Δt in the Knudsen cell from the equation

$$p = \frac{\Delta m}{KA\Delta t}\sqrt{\frac{2\pi RT}{M}} \tag{3}$$

where M is the molar mass of the substance; A is the area of the orifice; R is the universal gas constant; and T is the temperature in Kelvin. The Clausing factor K of the orifice was calculated using the relation[8]

$$K = 1 - 0.5\left(\frac{l}{r}\right) + 0.2\left(\frac{l}{r}\right)^2 \tag{4}$$

where l is the thickness of the foil and r is the radius of the orifice. The details of experimental parameters and the measured sublimation pressures are listed in Table 1.

The measured sublimation pressures at different temperatures were fitted to an Antoine type expression, with pressures in kPa and temperatures in K. Two parameters were found to be adequate to represent the data within experimental uncertainty.

$$\log(p/\text{kPa}) = A_i - B_i/(T/\text{K}) \tag{5}$$

The Antoine equation constants A and B determined for the best fitting are given in Table 2. The uncertainties are also listed. The results for anthracene and pyrene at different temperatures are shown in Figure 3 and Figure 4, respectively, as a function of $1/T$ as full lines. These substances have also been investigated by many workers and hence have well-known literature values, calculated from the vapor pressure equations given by the authors, which are also shown as points. The vapor pressures measured by us agree quite well with the data from the literature.[9−23] The enthalpy of sublimation derived from these vapor pressure values (from the slopes of the ln(p) vs $1/T$ plots) is (97.64 ± 1.27) $\text{kJ}\cdot\text{mol}^{-1}$ for anthracene and (103.25 ± 2.05) $\text{kJ}\cdot\text{mol}^{-1}$ for pyrene. These are in good agreement with the values reported in the literature[9−23] and reproduced in Table 2 for a ready reference. The sublimation enthalpies at 298.15 K derived from the above data using the method suggested by Chickos et al.[24] are also listed in Table 2. Chickos et al.[25] collected the available data for the enthalpy of sublimation at 298.15 K for anthracene and suggested the value 99.22 $\text{kJ}\cdot\text{mol}^{-1}$.

A number of sublimation/vapor pressure studies for [Cu(acac)$_2$] are found in the literature.[26−30] Three of these[26,27,30] are over a large temperature range [(315 to 453) K] but differ from each other considerably. The sample used by us was found to be free from moisture as shown by the isothermal and nonisothermal thermogravimetric analysis. The vapor pressure values for [Cu(acac)$_2$] measured by us are shown in Figure 5 as a function of $1/T$; some literature values are also included. The enthalpy of sublimation derived from the vapor pressures is 121.6 $\text{kJ}\cdot\text{mol}^{-1}$ [(363 to 443) K]. Due to the absence of heat capacity data for [Cu(acac)$_2$], the sublimation enthalpies at 298.15 K could not be calculated.

Some typical literature values are 116.6 $\text{kJ}\cdot\text{mol}^{-1}$ (298 K),[31] 120 $\text{kJ}\cdot\text{mol}^{-1}$ (298 K),[28] 57.1 $\text{kJ}\cdot\text{mol}^{-1}$ (298 K),[26] 79.9 $\text{kJ}\cdot\text{mol}^{-1}$ [(353 to 453) K],[27] and (108.2 ± 4.9) $\text{kJ}\cdot\text{mol}^{-1}$ [(443 to 498) K].[32] These and some other literature values[33−35] are listed in Table 2 together with our values and the parameters for eq 5. It is observed that the values range from (57 to 120) $\text{kJ}\cdot\text{mol}^{-1}$, and the picture is not satisfactory. Our value agrees with the value measured accurately with a microcalorimeter.[27]

Ribeiro de Silva et al.[36] and Bykov et al.[3] measured the sublimation pressure of [Ru(acac)$_3$] over the temperature range [(398 to 413) K] and [(423 to 493) K], respectively. Ribeiro de Silva et al.[36] also used the Knudsen cell method for the vapor pressure measurements. They synthesized [Ru(acac)$_3$] in the laboratory and purified it by crystallization from benzene. Its melting point was reported to be 260 °C, and at this temperature it started to decompose. A recent study[37] with a laboratory synthesized sample reports the decomposition even at low temperatures. Bykov et al.[3] used the gas saturation method for

Table 1. Details of Knudsen Cell Measurements

temp K	time s	vacuum mbar	orifice diameter mm	Clausing Factor	mass evaporated mg	vapor pressure Pa
			Anthracene			
389.05	3690	≈ 10^{-7}	0.516	0.878443	17.38	8.75
389.05	4168				21.58	9.62
393.75	4017				26.03	12.11
393.75	3600				23.93	12.43
398.55	4428				42.78	18.13
398.55	3420				33.62	18.5
376.95	7110	≈ 10^{-7}	0.656	0.902402	23.4	3.58
386.45	4860				35.81	8.13
365.66	10332	≈ 10^{-7}	0.678	0.905283	16.34	1.58
373.95	8784				26.98	3.11
392.95	6012				86.28	14.86
339.25	55620	≈ 10^{-7}	0.691	0.906907	6.25	0.104
348.35	14832				4.57	0.289
383.95	12780				7.76	0.577
360.45	4230	≈ 10^{-7}	0.715	0.909766	4.65	0.978
369.85	4680				9.43	1.18
379.55	4348				19.84	4.16
398.05	3384				63.93	17.65
			Pyrene			
408.05	4017	≈ 10^{-7}	0.416	0.854382	39.27	27.31
402.05	4500	≈ 10^{-7}	0.691	0.906907	78.95	16.62
392.95	6804				61.53	8.46
383.95	5904				30.48	4.72
373.95	11520				18.6	1.47
341.45	54540	≈ 10^{-7}	0.715	0.909766	5.08	0.075
351.05	54630				11.38	0.171
369.85	7740				8.07	0.882
379.55	5760				13.34	1.97
389.05	4050				25.17	5.39
398.55	3449				41.91	10.67
			$[Cu(acac)_2]$			
367.65	61200	≈ 10^{-7}	0.715	0.909766	18.3	0.022
405.05	6120				9.31	1.18
414.35	5508				18.04	2.57
423.85	6149				37.06	4.79
433.65	6660				76.66	9.27
442.85	4608				113.51	19.9
386.45	59400				13.52	0.172
395.55	18648				9.67	0.398
376.95	64836				5.93	0.068
400.64	15480				14.1	0.705
381.83	63645				9.3	0.11
372.42	66096				3.5	0.039
403.26	7020	≈ 10^{-7}	0.703	0.908358	7.64	0.875
417.53	4260				20.17	3.87
388.98	11760	≈ 10^{-7}	0.751	0.913741	3.44	0.201
398.50	4680				4.04	0.601
			$[Ru(acac)_3]$			
393.75	180420	≈ 10^{-7}	0.719	0.910225	8.80	0.029
398.51	64152				4.02	0.038
403.26	83448				7.75	0.057
408.02	27144	≈ 10^{-7}	0.715	0.909766	4.56	0.106
417.54	7812				5.40	0.443
422.30	9432				8.66	0.592
427.15	7452				10.24	0.891
431.81	6156				13.17	1.395
436.57	3816				10.71	1.84
441.33	3564		0.719		19.41	3.53
408.02	72540	≈ 10^{-7}	0.715	0.913741	14.97	0.117
417.53	8160				5.02	0.355
412.78	13860				4.95	0.250
431.81	6240				15.0	1.413

vapor pressure measurements for a sample synthesized in the laboratory and purified by the zone sublimation method (the reported melting point was 240 °C). In both studies, the purity of the samples was not mentioned. In the present study, the measured vapor pressure values for the moisture-free substance were lower than both of these values, the reasons for the discrepancy not being clear. However, the vapor pressures of the reference substances were very well reproduced several times with the current setup, which makes us trust that the quality of the present data is high.

The vapor pressure values at different temperatures are shown in Figure 6. These were also fitted to an Antoine type expression, with pressures P in kPa and temperature T in K. The parameters

Table 2. Constants for Equation 5 and the Sublimation Enthalpies

			$\Delta_{\mathrm{sub}}H_{\mathrm{m}}$	temp range
substance	A_i	B_i	$\mathrm{kJ \cdot mol^{-1}}$	K
anthracene	11.09 ± 0.21	5100.00 ± 80.66	97.64 ± 1.27*	(339 to 399)
			98.19*	(298)
			100.0 ± 2.8[a]	(318 to 363)
			94.6[b]	(354 to 399)
			96.8[b]	(298)
			98.5[c]	(342 to 353)
			94.8[d]	(358 to 392)
			98.5 ± 3.3[e]	(322 to 348)
			100.4 ± 1[f]	(337 to 360)
			102.6[g]	(313 to 363)
			103.9[g]	(298)
			103.4[h]	(303 to 373)
			99.22[i]	(298)
pyrene	11.62 ± 0.34	5393.20 ± 131.75	103.25 ± 2.05*	(341 to 418)
			104.46*	(298)
			103.1 ± 6.5[a]	(308 to 398)
			97.7[j]	(353 to 413)
			101.04[j]	(298)
			91.2[k]	(283 to 323)
			93.9[l]	(345 to 358)
			100.5[h]	(298 to 363)
			100.2[m]	(298)
[Cu(acac)$_2$]	12.68 ± 0.22	6350.2 ± 90.58	121.56 ± 1.40*	(363 to 443)
			116.6 ± 2[n]	(298)
			79.9[o]	(353 to 453)
			120[p]	(298)
			57.0 ± 1[q]	(298)
			109.5 [r]	(368 to 433)
			105.3 ± 9[s]	(413 to 483)
			106.1[t]	(335 to 361)
			115.1 ± 2.1[u]	(315 to 386)
			108.2 ± 4.9[v]	(443 to 498)
[Ru(acac)$_3$]	15.16 ± 0.52	7772.05 ± 220.24	148.81 ± 1.68*	(394 to 441)
			139.7 ± 2.5[w]	(398 to 413)
			127.0 ± 0.9[x]	(423 to 493)

* This work. [a] Ref 12. [b] Ref 9. [c] Ref 10. [d] Ref 11. [e] Ref 15. [f] Ref 16. [g] Ref 14. [h] Ref 23. [i] Ref 25. [j] Ref 21. [k] Ref 19. [l] Ref 20. [m] Ref 22. [n] Ref 31. [o] Ref 27. [p] Ref 28. [q] Ref 26. [r] Ref 33. [s] Ref 34. [t] Ref 35. [u] Ref 30. [v] Ref 32. [w] Ref 36. [x] Ref 3.

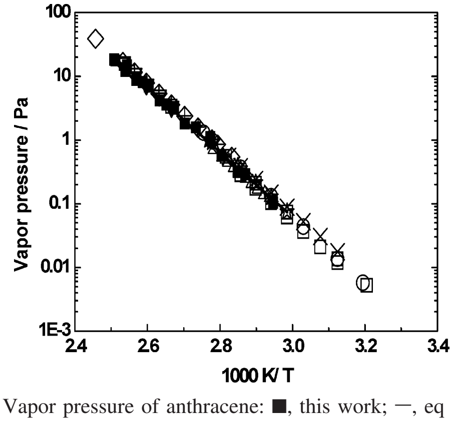

Figure 3. Vapor pressure of anthracene: ■, this work; —, eq 5; ◇, ref 9; Δ, ref 10; +, ref 11; □, refs 12 and 15; ×, ref 13; ○, ref 14; ☆, ref 16; ▽, ref 17.

for eq 5 are shown in Table 2 together with the derived enthalpy of sublimation.

The thermogravimetric experiments with the substances anthracene, pyrene, [Cu(acac)$_2$], and [Ru(acac)$_3$] were performed at different temperatures (three to five isotherms) in a nitrogen (and/or helium) gas atmosphere. The products of vapor pressure and the binary diffusion coefficient of various substances in the carrier gas were calculated from the experimental mass loss (Δm) for the time t using the relation derived previously[1]

$$p_{\mathrm{A}}^{\mathrm{vap}} D_{\mathrm{AB}} = \{(h+H)^2 - H^2\}\frac{RT\rho_{\mathrm{A}}}{2Mt} = \left\{\left(\frac{\Delta m}{S\rho_{\mathrm{A}}} + H\right)^2 - H^2\right\}\frac{RT\rho_{\mathrm{A}}}{2Mt} \tag{6}$$

Here T is the temperature; R is the universal gas constant; and ρ_{A} is the apparent density of the evaporating substance of molecular mass M. H is the initial distance between the surface (of surface area S) of the material and the top of the crucible in the thermogravimetric experiments. The experimental vapor pressure determined from the Knudsen effusion method was then used to derive the diffusion coefficient.

Figure 7 shows the diffusion coefficients of anthracene in nitrogen and in helium as a function of temperature. The maximum, minimum, and the mean values for at least three runs are shown. As expected, the binary diffusion coefficients in helium are throughout higher than in nitrogen. Gustafson and Dickhut[38] measured the diffusion coefficients of anthracene in

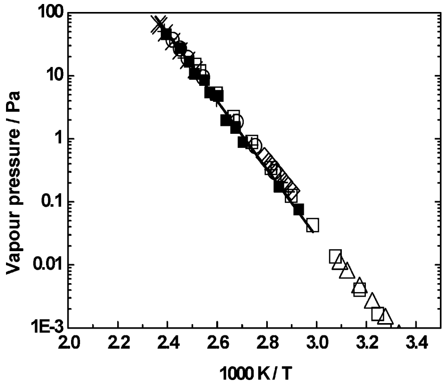

Figure 4. Vapor pressure of pyrene: ■, this work; —, eq 5; □, ref 12; ○, ref 18; Δ, ref 19; ◇, ref 20; +, ref 21; ×, ref 22.

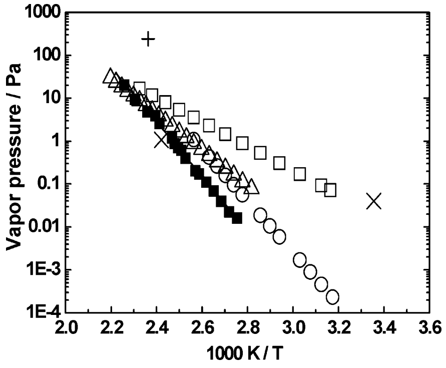

Figure 5. Vapor pressure of [Cu(acac)$_2$]: ■, this work; —, eq 5; □, ref 26; Δ, ref 27; +, ref 28; ×, ref 29; ○, ref 30.

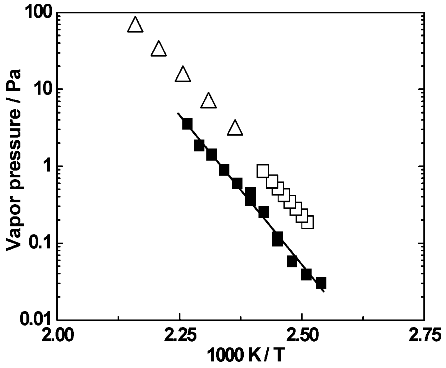

Figure 6. Vapor pressure of [Ru(acac)$_3$]; ■, this work; —, eq 5; □, ref 36; Δ, ref 3.

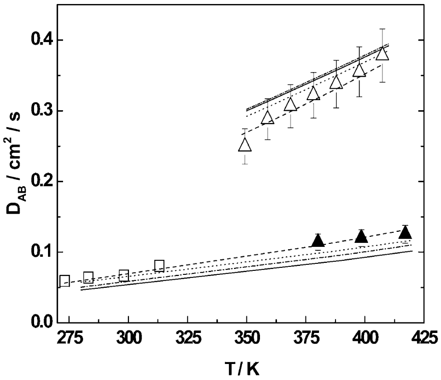

Figure 7. Diffusion coefficient of anthracene at various temperatures: Δ, mean value (helium); ▲, mean value (nitrogen); - - -, eq 10 and eq 11; —, eq 7; — • — • —, eq 8; •••••, eq 9; □, ref 38.

air at (0, 10, 25, and 40) °C. Their values are also shown in the graph. Mack[39] reported a value of 0.0783 for D_{12} of anthracene in air which has been questioned by other workers.[40]

For organic molecules, the binary diffusion coefficients in gases can be estimated with different methods given in the literature.[41] Some of these are:

(a) The Chapman−Enskog method derived from the kinetic theory of gases[41]

$$D_{\mathrm{AB}} = \frac{0.00266 T^{3/2}}{p M_{\mathrm{AB}}^{1/2} \sigma_{\mathrm{AB}}^{2} \Omega_{\mathrm{D}}} \qquad (7)$$

Here p is the pressure in bar; T is the temperature in K; $M_{\mathrm{AB}} = 2/(1/M_{\mathrm{A}} + 1/M_{\mathrm{B}})$ where M_{A} and M_{B} are the molecular masses of substance A and the carrier gas B. The characteristic length σ_{AB} in Angstrom units and the diffusion collision integral Ω_{D} can be calculated by selecting an intermolecular force law, e.g., Lennard-Jones. These were then ultimately calculated from the critical parameters of substances available in textbooks.[41]

(b) The correlation of Wilke and Lee[41]

$$D_{\mathrm{AB}} = \frac{[3.03 - (0.98/M_{\mathrm{AB}}^{1/2})](10^{-3}) T^{3/2}}{p M_{\mathrm{AB}}^{1/2} \sigma_{\mathrm{AB}}^{2} \Omega_{\mathrm{D}}} \qquad (8)$$

where the symbols have the same meaning as above.

(c) The method of Fuller et al.[41]

$$D_{\mathrm{AB}} = \frac{0.00143 T^{1.75}}{p M_{\mathrm{AB}}^{1/2} \left[\left(\sum_{v} \right)_{\mathrm{A}}^{1/3} + \left(\sum_{v} \right)_{\mathrm{B}}^{1/3} \right]^{2}} \qquad (9)$$

with the same symbols as above, and $\sum_v$ is the summation of atomic diffusion volumes of the groups which form the substance. These atomic volumes were determined from the regression of data for many substances and are available in the literature.[41]

The binary diffusion coefficients calculated with eqs 7 to 9 are also shown in Figure 7. All three methods give similar results which do not differ much from each other. The experimental values also agree with these values within experimental uncertainty. From simple gas kinetic theory, a T^n dependence with $n = 1.75$-2 is expected.[41] A curve with $n = 2$ is also included in the diagram. The diffusion coefficients obtained in this study do not differ appreciably from those calculated with different methods.

The diffusion coefficients of pyrene in nitrogen and in helium are shown in Figure 8 as a function of temperature. The maximum, minimum, and the mean values for at least three runs are shown. The diffusion coefficients from the literature[38] and the correlations [eqs 7 to 9] are also shown. As the critical parameters for pyrene were not available in the literature, these were calculated using the correlations suggested in the literature.[41] The discrepancies are larger here but acceptable. The binary diffusion coefficients in helium are throughout higher than in nitrogen.

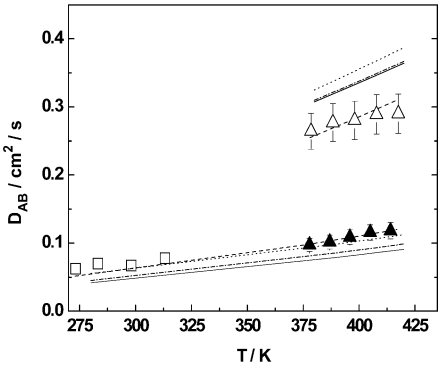

Figure 8. Diffusion coefficient of pyrene at various temperatures: Δ, mean value (helium); ▲, mean value (nitrogen); ----, eq 12 and eq 13; —, eq 7; — • — • —, eq 8; ••••, eq 9; □, ref 38.

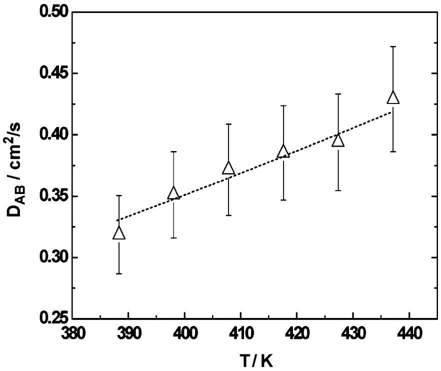

Figure 9. Diffusion coefficient of [Cu(acac)$_2$] at various temperatures: Δ, mean value (helium); - - -, eq 14.

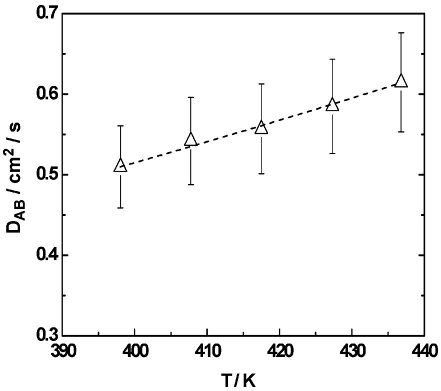

Figure 10. Diffusion coefficient of [Ru(acac)$_3$] at various temperatures: Δ, mean value(helium); - - -, eq 15.

Figure 9 shows the gaseous diffusion coefficients of [Cu(acac)$_2$] in helium. The results for [Ru(acac)$_3$] in helium are shown in Figure 10. The maximum, minimum, and the mean values for at least three runs are shown. No correlations are yet available for the estimation of the binary gaseous diffusion coefficients of organometallic compounds, hence these could not be calculated. The mass loss rate at lower temperatures in nitrogen was quite small, and hence the diffusion coefficients were not determined in a nitrogen mixture. The maximum, minimum, and the mean values for at least three runs are shown.

The measured diffusion coefficients can be represented within experimental uncertainty by the following equations

$$D_{AB}\ (\mathrm{cm^2 \cdot s^{-1}}) = 2.20 \cdot 10^{-6} T^2 \quad \text{(for anthracene in helium)} \tag{10}$$

$$D_{AB}\ (\mathrm{cm^2 \cdot s^{-1}}) = 7.56 \cdot 10^{-7} T^2 \quad \text{(for anthracene in nitrogen)} \tag{11}$$

$$D_{AB}\ (\mathrm{cm^2 \cdot s^{-1}}) = 1.784 \cdot 10^{-6} T^2 \quad \text{(for pyrene in helium)} \tag{12}$$

$$D_{AB}\ (\mathrm{cm^2 \cdot s^{-1}}) = 6.899 \cdot 10^{-7} T^2 \quad \text{(for pyrene in nitrogen)} \tag{13}$$

$$D_{AB}\ (\mathrm{cm^2 \cdot s^{-1}}) = 2.193 \cdot 10^{-6} T^2 \quad \text{(for [Cu(acac)}_2\text{] in helium)} \tag{14}$$

$$D_{AB}\ (\mathrm{cm^2 \cdot s^{-1}}) = 3.218 \cdot 10^{-6} T^2 \quad \text{(for [Ru(acac)}_3\text{] in helium)} \tag{15}$$

This temperature dependence of the diffusion coefficient is also shown in the respective diagrams (Figures 7 to 10).

4. Summary

Some organometallic compounds, which are often used as CVD precursors, were investigated. It was found that [V(acac)$_3$], [Zn(acac)$_2$], [Tm(acac)$_3$], and [Dy(acac)$_3$] start to decompose at typical evaporator conditions. [Cu(acac)$_2$] and [Ru(acac)$_3$] are stable, and hence their vapor pressures were measured over a large temperature range. The vapor pressures and the derived sublimation enthalpies have been compared with the available literature values. The diffusion coefficients of these organometallic compounds were also measured combining these vapor pressure data with thermogravimetric measurements. The diffusion coefficients for these organometallic substances present the possibility of calculating the behavior of these precursors. This reliable data for the vapor pressures and the diffusion coefficients of two reference substances, viz., anthracene and pyrene, are also reported at different temperatures.

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