

of such clays in sustained release and waste control applications.

There are at least two sites for bound TEP, which could be explained as either internal and external TEP, or perhaps more probably interlamellar TEP in two distinct environments bound to the magnesium.

However, in each case TEP is bound through one oxygen, probably to a cation.<sup>10</sup> The quantity of bound material can be estimated as about 10% w/w (100 mg/g). The achievable detection limit depends very much on line width, and paramagnetic-free clays (synthetic) would be useful for such work. However, our study serves to show that a great deal of information concerning the nature of organic molecules absorbed and adsorbed by clays can be obtained by solid-state NMR methods.

### Experimental Section

**Materials.** Surrey Finest (fuller's earth) was characterized by a water content of 12% w/w (by TGA) and a  $d(001)$  spacing of 14.7 Å, characteristic of two layers of intercalated water.<sup>4</sup> Westonite was characterized by a water content of 13% w/w (by TGA) and a  $d(001)$  spacing of 14.7 Å, characteristic of two layers of intercalated water. Samples were prepared by grinding TEP with the solid clay until the sample appeared homogeneous. Triethyl phosphate was purchased from British Drug Houses, dried over molecular sieves, and distilled before use. Purity was confirmed by high-resolution solution <sup>13</sup>C and <sup>31</sup>P NMR spectroscopies.

**Instrumentation.** ESR spectra were recorded with a Bruker ERD 2000/10 at room temperature: water content was estimated by thermogravimetry with a Stanton Redcroft TG-750 TGA.

NMR spectra were recorded with a Bruker MSL-300 instrument with <sup>1</sup>H, <sup>13</sup>C, and <sup>31</sup>P frequencies of 300.13, 75.47, and 121.49 MHz, respectively. No line broadening was applied to any spectra. <sup>1</sup>H and <sup>13</sup>C shifts are in ppm relative to liquid TMS, <sup>31</sup>P are measured in ppm relative to 85% phosphoric acid by replacement.

<sup>13</sup>C spectra were referenced by replacement to the methylene peak of solid adamantane, to give a scale equivalent to TMS.<sup>24</sup>

The probe dead time for <sup>1</sup>H MAS spectra was approximately 6 ms, so broad features (>30 kHz) will be distorted or attenuated. <sup>31</sup>P spectra were recorded in MAS experiments typically: 2000 scans, a 10 s delay, 4-ms acquisition time. CP-MAS experiments were typically: 10 000 scans, a 5-s delay, an acquisition time of 16 ms, and a contact time of 1 ms. In both cases the sweep width was 125 kHz with 70-kHz proton decoupling. <sup>13</sup>C spectra were recorded in single-pulse magic angle spinning experiments, with typical conditions: 400 scans, a 10-s recycle delay, and 34-ms acquisition time. Cross-polarization magic angle spinning experiments (CP-MAS) were typically: 2000 scans, a 2-s delay, an acquisition time of 34 ms, and a contact time of 1 ms. In both cases the sweep width was 30 kHz with 70-kHz proton decoupling.

The <sup>13</sup>C Hartmann-Hahn condition was set by using slowly spinning adamantane (ca. 1.5 kHz). The match position for this is sensitive to changes of ca. 5% in either the <sup>1</sup>H or <sup>13</sup>C radio frequency field. The <sup>31</sup>P match was found by using slowly spinning NH<sub>4</sub>H<sub>2</sub>PO<sub>4</sub>. The signal strength is less sensitive to mismatch than adamantane/<sup>13</sup>C, but the <sup>1</sup>H and <sup>31</sup>P fields are likely to be equal within 20%.

Experiments to assess the quantities of bound material were carried out at different times during the study and are at best semiquantitative. The absolute intensity mode was used, with due allowance for differences in the number of scans; arbitrary intensity is plotted in terms of the peak area (see Figures 1 and 4).

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**Registry No.** TEP, 78-40-0; montmorillonite, 1318-93-0.

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## Vaporization Processes of Aluminum $\beta$ -Diketone Chelates

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Aluminum(III) trifluoro- and hexafluoroacetylacetonates, Al(C<sub>5</sub>H<sub>4</sub>F<sub>3</sub>O<sub>2</sub>)<sub>3</sub> and Al(C<sub>5</sub>HF<sub>6</sub>O<sub>2</sub>)<sub>3</sub>, were prepared by reaction of aluminum isopropoxide with the corresponding fluorinated acetylacetonate in benzene solution. The kinetics of vaporization of these fluorinated aluminum complexes and aluminum(III) acetylacetonate, Al(C<sub>5</sub>H<sub>7</sub>O<sub>2</sub>)<sub>3</sub>, was investigated by isothermal thermogravimetry at temperatures ranging from 70 to 190 °C with an hydrogen or argon pressure varying between 100 and 300 Torr. The vaporization process was found to be rate-limited by the diffusion of these large complex molecules in the buffer gas (H<sub>2</sub> or Ar). The activation energy of these processes was demonstrated to be equal to the standard enthalpy of sublimation or evaporation of metal complexes. The values of the standard enthalpy of sublimation or evaporation of aluminum(III) complexes were compared with those reported in the literature and determined by other techniques. A comparison of the volatility of these metal complexes in terms of mass of aluminum evolved in the gas phase per minute as a function of vaporization temperature is also presented in this paper and can serve as a guideline for the selection of a suitable precursor in chemical vapor deposition of aluminum-containing films.

### Introduction

Metal complexes and organometallic compounds such as metal alkyls, metal alkoxides,  $\beta$ -diketonates, and cyclopentadienyl derivatives are under intensive investigation since these compounds are attractive candidates to be used as volatile precursors in chemical vapor deposition (CVD) of ceramic materials, new superconductors, and other

various insulating or conductive thin films.<sup>1-5</sup> Aluminum acetylacetonate, Al(C<sub>5</sub>H<sub>7</sub>O<sub>2</sub>)<sub>3</sub> or Al(acac)<sub>3</sub>, appears as an

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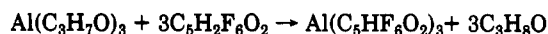
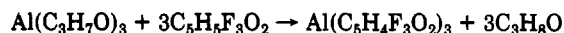
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appropriate volatile compound for deposition of aluminum oxide films<sup>6,7</sup> as well as for preparation of submicron-size  $\text{Al}_2\text{O}_3$  powder.<sup>8</sup> The properties of the  $\text{Al}_2\text{O}_3$  films deposited by pyrolysis of  $\text{Al}(\text{acac})_3$  at low temperatures (250–700 °C) were found to be suitable for microelectronic applications in particular for use as insulating and passivating films in the production of discrete elements and integrated circuits. The major features related to the use of an organometallic compound as a CVD precursor include the vaporization rate of the compound, the thermal stability, and the chemical inertness with respect to water vapor or air (hygroscopic and pyrophoric nature of the compound). Various metal  $\beta$ -diketone chelates were investigated by thermogravimetry under nonisothermal conditions for rapid determination of their relative volatility.<sup>9</sup> The order of increasing volatility of the aluminum(III)  $\beta$ -diketonates was observed to be  $\text{Al}(\text{C}_5\text{HF}_6\text{O}_2)_3 > \text{Al}(\text{C}_5\text{H}_4\text{F}_3\text{O}_2)_3 > \text{Al}(\text{C}_5\text{H}_7\text{O}_2)_3$ . In other words, the volatility of these metal complexes increases with increasing fluorine substitution in the chelate ligand. However, the kinetic data (e.g., vaporization rate, activation energy) and mechanism of the vaporization process were not deduced or elucidated from this nonisothermal thermogravimetric analysis.

In the present paper are reported the results related to the kinetics of sublimation or evaporation of aluminum(III) acetylacetonate,  $\text{Al}(\text{acac})_3$ , trifluoroacetylacetonate,  $\text{Al}(\text{tfacac})_3$ , and hexafluoroacetylacetonate,  $\text{Al}(\text{hfacac})_3$ , in hydrogen or argon ambient. The fluorinated compounds were prepared from aluminum isopropoxide,  $\text{Al}(\text{CH}_3\text{CH}(\text{OCH}_3)_2)_3$ , and the corresponding diketone in benzene solution. The vaporization rate of these aluminum(III)  $\beta$ -diketone chelates was investigated as a function of the vaporization temperature and pressure of the buffer gas ( $\text{H}_2$  or Ar). The values of standard enthalpy of sublimation or evaporation deduced from the kinetic data were compared with the values reported in the literature.

### Experimental Section

The powdery aluminum(III) acetylacetonate,  $\text{Al}(\text{C}_5\text{H}_7\text{O}_2)_3$ , with a purity of 99% was supplied by Aldrich Chemical Co. The experimental procedure adopted for the preparation of aluminum(III) fluorinated  $\beta$ -diketonates,  $\text{Al}(\text{C}_5\text{H}_4\text{F}_3\text{O}_2)_3$  and  $\text{Al}(\text{C}_5\text{HF}_6\text{O}_2)_3$ , was derived from the method proposed by Fay and Piper.<sup>10</sup> This method is based on the reaction in benzene solution between aluminum isopropoxide,  $\text{Al}(\text{C}_3\text{H}_7\text{O})_3$ , and trifluoro or hexafluoroacetylacetonate in stoichiometric proportion:



Fluorinated acetylacetonate (0.06 mol) was added to a solution of aluminum isopropoxide (0.02 mol) in 40 cm<sup>3</sup> of benzene. The reaction occurred at room temperature and was almost complete within 4 h. Propanol produced by the reaction and benzene as

**Table I. Major Peaks in the X-ray Diffraction Pattern of Aluminum(III) Trifluoroacetylacetonate Produced by Reaction between 1,1,1-Trifluoro-2,4-pentanedione and Aluminum Isopropoxide**

interplanar dist <i>d</i> , Å	peak intensity, %	ASTM data <sup>a</sup>	
		interplanar dist <i>d</i> , Å	peak intensity, %
9.84	40.8	9.95	40
7.01	32	7.11	20
6.43	47	6.48	90
4.86	18	4.91	40
4.44	25	4.47	40
3.99	100	4.03	100
3.33	12	3.33	20

<sup>a</sup> ASTM data are reported from ref 10.

**Table II. Major Absorption Bands in the Infrared Spectrum of Aluminum(III) Hexafluoroacetylacetonate Produced by Reaction between 1,1,1,5,5,5-Hexafluoroacetylacetonate and Aluminum Isopropoxide**

present work, cm <sup>-1</sup>	data from ref 12	
	cm <sup>-1</sup>	vibration mode
1660	1654	C=O stretching
1623	1636	C=C stretching
1570	1578	C=O stretching
		CH bending
1545	1552	
1490	1483	
1446		
1372	1370	C-C stretching
		CF <sub>3</sub> stretching
1257	1262	CF <sub>3</sub> stretching
1209	1222	
1162	1162	CH in-plane bending
1142		
1120		
	1048	
947		
864		
832		
811	816	CH out-of-plane bending
747	748	C-CF <sub>3</sub> stretching
669	672	
593		

well as unreacted residual fluorinated acetylacetonate (liquid at room temperature) were removed by vacuum distillation at room temperature, and aluminum(III)  $\beta$ -diketonates precipitated in the reaction vessel. The yield of aluminum chelate was higher than 90 wt %, in agreement with the value of 91 wt % reported in the literature.<sup>10</sup> The precipitates of aluminum(III) fluorinated  $\beta$ -diketonate were rinsed several times with pure benzene to eliminate the major part of unreacted aluminum isopropoxide and fluorinated acetylacetonate. Then, the aluminum(III) fluorinated acetylacetonates were purified by vacuum evaporation of residues (aluminum isopropoxide, acetylacetonate, propanol, and benzene) at temperatures in the range 60–70 °C. During this purification step, the traces of fluorinated acetylacetonate, propanol, and benzene were completely removed from the solid compound. The residue of aluminum isopropoxide was partially eliminated since the vapor pressure of this aluminum compound<sup>11</sup> is of the same order of magnitude than that of fluorinated aluminum(III)  $\beta$ -diketonates; the content of aluminum isopropoxide residue in fluorinated aluminum chelates was evaluated to be less than 5% from the yield of the synthesis reaction. The presence of this impurity leads to a negligible deviation in the vaporization rate of fluorinated aluminum chelates compared with the uncertainty on the experimental measurements of the mass loss of samples by thermogravimetry. After purification, the white crystalline product

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Table III. Melting Points of Aluminum(III)  $\beta$ -Diketone Chelates

ref	year	melting point, °C		
		Al(acac) <sub>3</sub>	Al(tfacac) <sub>3</sub>	Al(hfacac) <sub>3</sub>
13	1972		125 <sup>a</sup>	71 <sup>a</sup>
14	1972		123 <sup>b</sup>	74 <sup>b</sup>
15	1974	197 <sup>c</sup>		
16	1983	194.6 <sup>c</sup>		
17	1988	191–195 <sup>c</sup>		71–76 <sup>c</sup>

<sup>a</sup> Deduced from the change in slope of vapor pressure vs  $1/T$  curves given in Figure 2 ref 13. <sup>b</sup> Deduced from the change in slope of vapor pressure vs  $1/T$  curves. <sup>c</sup> Determined by differential thermal analysis.

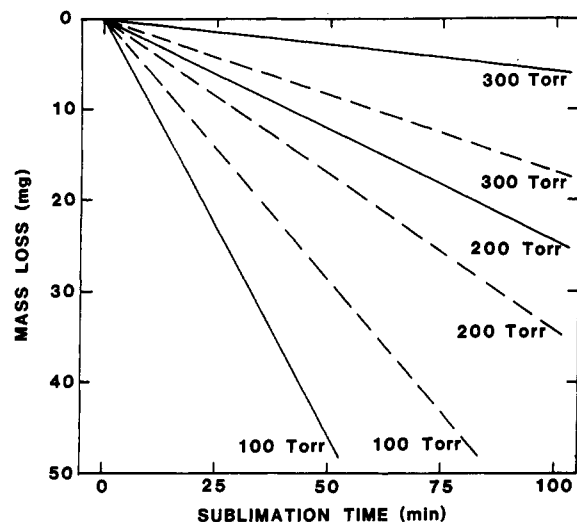


Figure 1. Typical thermogravimetric curves for sublimation of Al(acac)<sub>3</sub> at 160 °C under various pressures of argon (solid line) or hydrogen (dashed line) (1 Torr = 133 Pa).

was identified to be Al(C<sub>6</sub>H<sub>4</sub>F<sub>3</sub>O<sub>2</sub>)<sub>3</sub> and Al(C<sub>6</sub>HF<sub>6</sub>O<sub>2</sub>)<sub>3</sub> by X-ray diffraction technique and infrared absorption spectroscopy. The experimental X-ray pattern and IR absorption spectrum were similar to those given in the literature<sup>10,12</sup> (Tables I and II).

The kinetics of vaporization of aluminum chelates was investigated by thermogravimetry using an Uguine-Eyraud system, Model B-70. The thermogravimetric analyzer was equipped with facilities for isothermal and vacuum or reduced pressure operations. The mass loss of the boat containing 50–100 mg of metal complex was recorded as a function of time at constant temperature and pressure. The vaporization processes of Al(acac)<sub>3</sub>, Al(tfacac)<sub>3</sub>, and Al(hfacac)<sub>3</sub> were investigated at a temperature ranging from 70 to 190 °C with H<sub>2</sub> or Ar pressure varying between 100 and 300 Torr. The first 10–30 min of these experiments was needed for temperature stabilization of samples so that the mass loss occurring for this stabilization step was eliminated from the kinetic measurements.

## Results

**1. Sublimation of Al(acac)<sub>3</sub>.** In preliminary experiments, few milligrams of Al(acac)<sub>3</sub> were placed in the cylindrical boat (83 mm<sup>2</sup> cross-sectional area) of the thermogravimetric analyzer and were vaporized under 300 Torr of hydrogen or argon at temperatures lower than 190 °C. In this temperature range, the metal complex was solid, the melting point of Al(acac)<sub>3</sub> being slightly higher than 190 °C (Table III). The mass of the sample was recorded until a constant value was reached. At the end of these experiments, the boat was found to be empty; the mass loss of samples investigated between 120 and 190 °C was thereby demonstrated to result from the sublimation

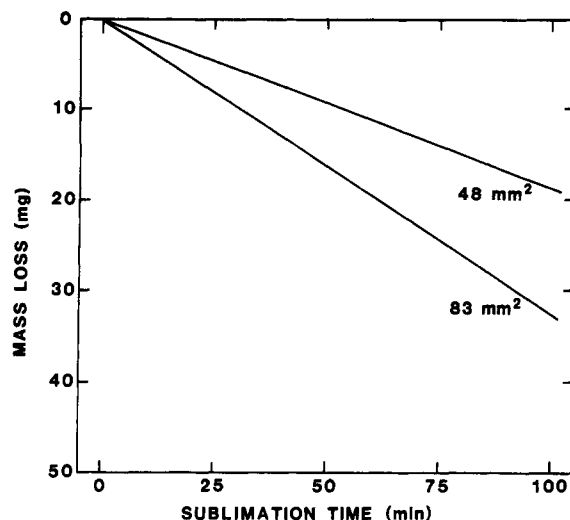


Figure 2. Effect of the cross-sectional area of the cylindrical boat on the kinetics of sublimation of Al(acac)<sub>3</sub> at 150 °C under 100 Torr of hydrogen.

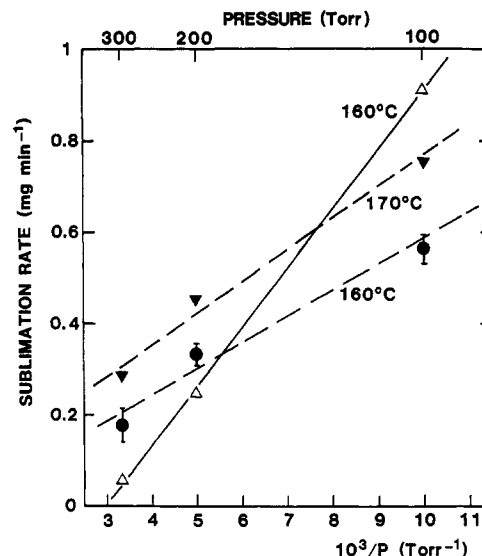


Figure 3. Pressure effect on the sublimation rate of Al(acac)<sub>3</sub> at various temperatures under argon (solid line) or hydrogen (dashed line).

of Al(acac)<sub>3</sub> without any decomposition leading to a solid residue.

Typical thermogravimetric curves giving the mass loss versus time are plotted in Figure 1. The sublimation rate of Al(acac)<sub>3</sub> deduced from the slope of the thermogravimetric curves was constant during the course of the experiment and decreased with increasing H<sub>2</sub> or Ar pressure. Furthermore, the mass loss of samples was observed to be proportional to the cross-sectional area of the boat (Figure 2).

The sublimation rate of Al(acac)<sub>3</sub> was inversely proportional to the H<sub>2</sub> or Ar pressure (Figure 3). At a given temperature, the deviation between the sublimation rates of the metal complex in H<sub>2</sub> and Ar ambient was dependent on the pressure value, e.g., at 160 °C and 180 Torr, this deviation is equal to zero (Figure 3).

The temperature effect on the sublimation rate of Al(acac)<sub>3</sub> in H<sub>2</sub> or Ar ambient is exhibited in the Arrhenius diagram given in Figure 4. The apparent activation energy of the sublimation process was found to be (15.5 ± 0.8) or (28.5 ± 1.2) kcal mol<sup>-1</sup> in hydrogen or argon ambient, respectively. At low temperatures for a given buffer gas pressure ranging from 100 to 300 Torr, the sublimation rate

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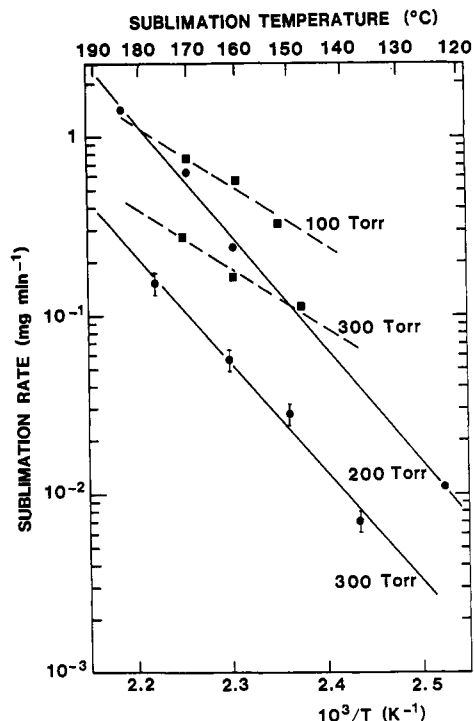


Figure 4. Arrhenius diagram for sublimation of  $\text{Al}(\text{acac})_3$  at various pressures of argon (solid line) or hydrogen (dashed line).

of  $\text{Al}(\text{acac})_3$  in hydrogen is higher than that in argon ambient. However, a reverse situation is observed in the high-temperature range since the activation energies (or the slope of Arrhenius curves) of the sublimation process under  $\text{H}_2$  and Ar are different by a factor of 2. The inversion temperature depends on the pressure of the buffer gas (Figure 4).

**2. Sublimation of  $\text{Al}(\text{tfacac})_3$  and Evaporation of  $\text{Al}(\text{hfacac})_3$ .** As in the case of  $\text{Al}(\text{acac})_3$ , preliminary experiments were carried out to demonstrate that the mass loss of samples resulted from the sublimation of  $\text{Al}(\text{tfacac})_3$  below  $110^\circ\text{C}$  and the evaporation of  $\text{Al}(\text{hfacac})_3$  at temperatures higher than  $70^\circ\text{C}$  (the melting points of these fluorinated metal complexes are reported in Table III). In fact, the kinetics of vaporization of these aluminum complexes was investigated in the same temperature range ( $70$ – $110^\circ\text{C}$ ). Typical thermogravimetric curves of the vaporization processes in  $\text{H}_2$  or Ar ambient are represented in Figure 5. The vaporization rates of  $\text{Al}(\text{tfacac})_3$  and  $\text{Al}(\text{hfacac})_3$  deduced from the slope of thermogravimetric curves were independent of time (or constant during the experiment) and were higher in hydrogen than in argon ambient.

The temperature effect on the vaporization rate of these fluorinated metal complexes is exhibited in the Arrhenius diagram plotted in Figure 6. The apparent activation energy was equal to  $(24.2 \pm 1.2)$  and  $(17.4 \pm 1.0)$   $\text{kcal mol}^{-1}$  for the sublimation of  $\text{Al}(\text{tfacac})_3$  and the evaporation of  $\text{Al}(\text{hfacac})_3$ , respectively. In addition, the values of these activation energies were independent of the nature of the buffer gas. At a given temperature and pressure of buffer gas, the sublimation rate of  $\text{Al}(\text{tfacac})_3$  (expressed in  $\text{mg min}^{-1}$ ) was higher than the evaporation rate of  $\text{Al}(\text{hfacac})_3$ , although the vapor pressure of  $\text{Al}(\text{hfacac})_3$  is higher by a factor of 10 than that of  $\text{Al}(\text{tfacac})_3$ .<sup>13</sup> However, the ac-

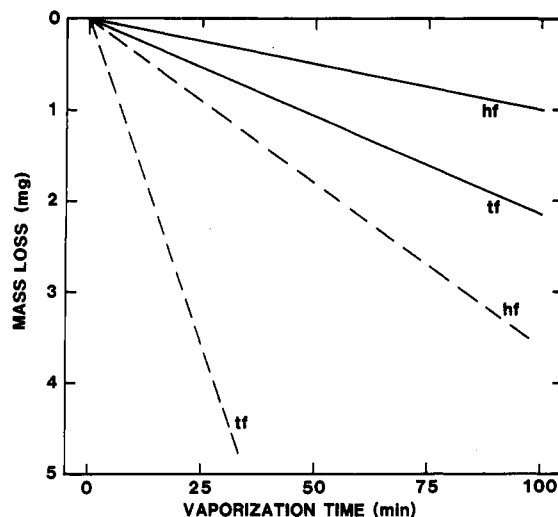


Figure 5. Typical thermogravimetric curves for the vaporization of  $\text{Al}(\text{tfacac})_3$  and  $\text{Al}(\text{hfacac})_3$  at  $95^\circ\text{C}$  under 100 Torr of argon (solid line) or hydrogen (dashed line).

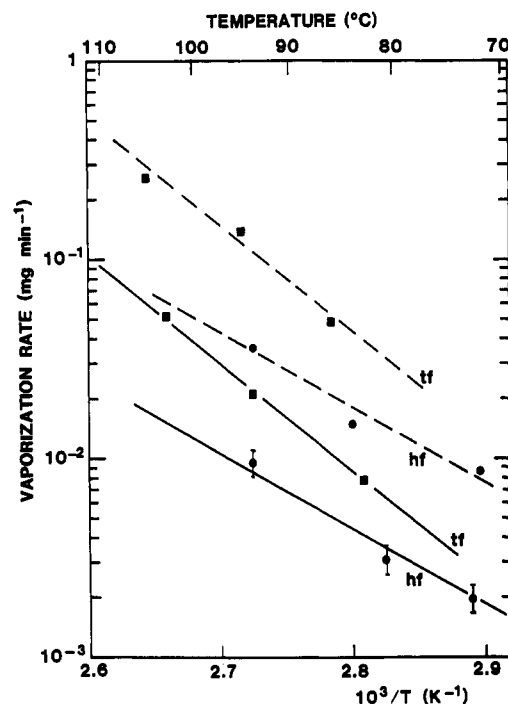


Figure 6. Arrhenius diagram for vaporization of  $\text{Al}(\text{tfacac})_3$  and  $\text{Al}(\text{hfacac})_3$  under 100 Torr of argon (solid line) or hydrogen (dashed line).

tivation energies of these processes being different, a reverse situation can be found at higher temperatures. The inversion temperature was dependent on the pressure and nature of the buffer gas.

## Discussion

**1. Sublimation of  $\text{Al}(\text{acac})_3$ .** Since the sublimation rate of  $\text{Al}(\text{acac})_3$  was proportional to the cross-sectional area of the boat (Figure 2) and independent of the initial mass of the sample, the kinetics of the sublimation process was independent of the specific surface area of the powdery material. In other words, the closely packed structure of the powdery sample (particle size of about  $1\ \mu\text{m}$ ) resulted in a sublimation zone strictly limited to the area of the

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Table IV. Enthalpy of Sublimation or Evaporation of Aluminum(III)  $\beta$ -Diketone Chelates

ref	year	enthalpy of sublimation (S) or evaporation (E), kcal mol <sup>-1</sup>			temp range, °C	exptl method
		Al(acac) <sub>3</sub>	Al(tfacac) <sub>3</sub>	Al(hfacac) <sub>3</sub>		
19	1960	4.52 (S) <sup>a</sup> 16.05 <sup>b</sup>	9.56 (S) <sup>a</sup>		150–230 <sup>c</sup>	vapor press.-temp measts by manometry
20	1965	4.58 (S)			65–165	vapor press.-temp measts by manometry
21	1968		9.56 (S) 17.8 ± 0.3 (E) <sup>d</sup>		45–120 121–148	vapor press.-temp measts by torsion effusion method
13	1972	23.7 (S) <sup>e</sup>	21.6 (S) <sup>e</sup> 17.5 (E) <sup>e</sup>	14.3 ± 0.2 (E) <sup>d</sup>	75–111 125–160 80–125 125–150	vapor press.-temp measts by torsion effusion method
14	1972	15.8 ± 0.8 (S)	22.4 ± 1.6 (S) 15.8 ± 0.8 (E)	25.0 (S) <sup>e</sup> 14.5 (E) <sup>e</sup>	50–71 71–110 110–140 80–122 123–150	vapor press.-temp measts by manometry
22	1965	25.1 (S) <sup>f</sup>	26.3 (S) <sup>f</sup>	26.2 ± 0.9 (S) 12.1 ± 0.3 (E)	50–74 74–110	effusion technique
23	1980	28.4 ± 1.9 (S)		22.4 (E) <sup>f</sup>	115–140	isoteniscopic method
24	1975	29.1 ± 1.0 (S) <sup>g</sup>				
26	1971	22.5 ± 1.4 (E)			190–270	DSC <sup>h</sup>
27	1981	11.3 ± 0.2 (S)			64–132	torsion effusion method
16	1983	30.05 ± 0.77 (S)			110–170	DSC
17	1988	24.4 ± 0.8 (S) 18.8 ± 0.2 (E)			160–191 195–242	DSC
this work		28.5 (S-Ar) 15.5 (S-H <sub>2</sub> )		18.6 ± 1.5 (S) 14.0 ± 0.2 (E)	50–71 76–138	thermogravimetry
			24.2 (S)		120–190 150–180	
				17.4 (E)	80–105 70–95	

<sup>a</sup>Data given in Table II of ref 19. <sup>b</sup>Deduced from the slope of the vapor pressure versus  $1/T$  curve given in Figure 2 of ref 19. <sup>c</sup>The temperature range encompassed the melting point. <sup>d</sup>Reported in Table I of ref 13 from data published in ref 21. <sup>e</sup>Deduced from the slope of vapor pressure versus  $1/T$  curves given in Figure 2 of ref 13. <sup>f</sup>Reported in Table III of ref 14 from data published in ref 22. <sup>g</sup>Reported in Table III of ref 24 from ref 25. <sup>h</sup>Differential scanning calorimetry.

macroscopic gas-solid interface, i.e., to the cross-sectional area of the cylindrical boat.

Three major successive steps can be involved in the sublimation mechanism of Al(acac)<sub>3</sub>, namely, (i) desorption of metal complex molecules from the surface of crystallites located on top of the powdery sample, (ii) diffusion of these molecules in the buffer gas from the boat to the cold wall of the thermogravimetric analyzer, and (iii) condensation of metal complex vapor on the cold wall. The diffusion of large complex molecules in the buffer gas may be the rate-limiting step of the sublimation process. Assuming that the kinetics of sublimation is mass-transport-limited, the mass loss,  $\Delta m$ , of the sample per cm<sup>2</sup> of the sublimation area was calculated as a function of time,  $t$ , pressure of buffer gas,  $P$ , and sublimation temperature,  $T$ :<sup>18</sup>

$$\Delta m = (k'/P)(RT)^{1/2} \exp[-(\Delta H/RT) + (\Delta S/R)]t \quad (1)$$

In eq 1  $k'$  is a constant,  $R$  is the ideal gas constant, and  $\Delta H$  and  $\Delta S$  are the standard enthalpy and standard entropy of sublimation of the metal complex, respectively. At a given temperature and pressure, eq 1 can be written as follows:

$$\Delta m = Kt \quad (2)$$

where  $K$  is a constant. Therefore, the mass loss predicted by the kinetic model is proportional to the vaporization time as was observed experimentally.

The sublimation rate,  $S_R$ , of the metal complex derived from eq 1 is given by

$$S_R = d(\Delta m)/dt = (k'/P)(RT)^{1/2} \exp[-(\Delta H/RT) + (\Delta S/R)] \quad (3)$$

At a given sublimation temperature, the sublimation rate

of the metal complex predicted by the kinetic model is inversely proportional to the buffer gas pressure and is in good agreement with the experimental kinetic law determined by thermogravimetry.

Furthermore, at a given buffer gas pressure, the sublimation rate of the metal complex can be expressed as a function of the sublimation temperature:

$$\log S_R = (-\Delta H/2.3RT) + 0.5 \log T + \text{constant} \quad (4)$$

In a narrow temperature range, the variation of the second term in the right-hand side of eq 4 is negligible with respect to that of the first term, and eq 4 can be written as follows:

$$\log S_R = (-\Delta H/2.3RT) + C' \quad (5)$$

As a result, the model proposed for the sublimation mechanism of a metal complex<sup>18</sup> leads to a sublimation rate complying with the Arrhenius law and an apparent activation energy (deduced from the slope of Arrhenius curves) equal to the standard enthalpy of sublimation or evaporation of the metal complex.

The apparent activation energy of sublimation of aluminum(III) acetylacetonate in H<sub>2</sub> or Ar ambient given in Table IV can be compared with the standard enthalpy of sublimation of the metal complex reported in the literature. The value of 28.5 kcal mol<sup>-1</sup> deduced from the kinetics of sublimation of the metal complex in Ar ambient is in good agreement with the value of the standard enthalpy of sublimation measured by differential scanning calorimetry.<sup>16,17</sup> The activation energy of the sublimation

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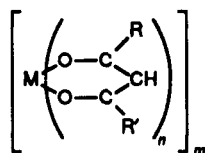
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of aluminum acetylacetonate in hydrogen was equal to 15.5 kcal mol<sup>-1</sup>, i.e., about one-half the value obtained in Ar ambient. This result suggests that dimer molecules, Al<sub>2</sub>(acac)<sub>6</sub>, and monomer molecules, Al(acac)<sub>3</sub>, may be involved in the sublimation process occurring in Ar and H<sub>2</sub> ambient, respectively. Schematically, the sublimation process can be represented as follows:

in argon aluminum complex (sol)  $\rightarrow$  Al<sub>2</sub>(acac)<sub>6</sub>(g)

in hydrogen aluminum complex (sol)  $\rightarrow$  Al(acac)<sub>3</sub>(g)

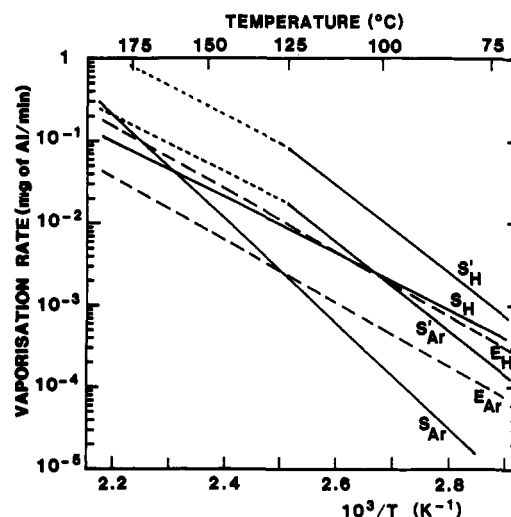
The existence of oligomers such as



where  $n$  is the valence number of metal M, R and R' are alkyl groups (CH<sub>3</sub>, C<sub>2</sub>H<sub>5</sub>, etc.) or fluorinated ligands (CM<sub>3</sub>, C<sub>3</sub>F<sub>7</sub>, etc.) has already been reported.<sup>28</sup> The degree,  $m$ , of oligomerization depends on mutual effects of ligand size and extent of fluorination of ligands.<sup>3</sup> In addition, the volatility of these metal complexes is enhanced by reducing oligomerization.

Interactions between H<sub>2</sub> molecules and aluminum complex molecules on the surface of crystallites as well as in the gas phase may lead to the formation of the monomeric derivative. As a result, the volatility of the aluminum complex is higher in hydrogen than in argon ambient since the diffusivity of a dimer molecule in the buffer gas is higher than that of a monomer molecule. Furthermore, the dimerization of aluminum acetylacetonate, i.e., the sublimation of Al<sub>2</sub>(acac)<sub>6</sub> molecules could explain the discrepancy observed for the values of the standard enthalpy of sublimation deduced from vapor pressure-temperature measurements by manometry or torsion effusion method; the enthalpy of sublimation was found to vary from 11.3 to 25.1 kcal mol<sup>-1</sup> (Table IV). The value of 4.58 kcal mol<sup>-1</sup> can be disregarded since in these experiments the vapor phase was partially soluble in the manometric liquid fluid.<sup>19,20</sup>

**2. Sublimation of Al(tfacac)<sub>3</sub> and Evaporation of Al(hfacac)<sub>3</sub>.** The vaporization mechanism proposed for the sublimation of metal complexes,<sup>18</sup> in particular for Cu(acac)<sub>2</sub> and Al(acac)<sub>3</sub>, can be invoked to interpret the kinetic data of vaporization of the fluorinated aluminum complexes, i.e., the kinetics of vaporization may be mass-transport-limited. The vaporization rate of the fluorinated compounds was enhanced by substituting hydrogen for argon since the diffusivity of these large complex molecules was higher in the buffer gas with a lower molar mass. The apparent activation energy of the vaporization process was independent of the nature of the buffer gas. Accordingly, the complex molecules evolved by the vaporization process were of the same nature in H<sub>2</sub>



**Figure 7.** Vaporization rate of aluminum(III)  $\beta$ -diketonates versus temperature under 100 Torr of buffer gas. Solid lines: sublimation rate of Al(acac)<sub>3</sub> in argon (curve S<sub>Ar</sub>) or hydrogen (curve S<sub>H</sub>) and sublimation rate of Al(tfacac)<sub>3</sub> in argon (curve S'<sub>Ar</sub>) or hydrogen (curve S'<sub>H</sub>). Dashed lines: evaporation rate of Al(hfacac)<sub>3</sub> in argon (curve E<sub>Ar</sub>) or hydrogen (curve E<sub>H</sub>). Dotted lines: evaporation rate of Al(tfacac)<sub>3</sub> in argon or hydrogen plotted assuming that the activation energy of the evaporation process is equal to the standard enthalpy of evaporation given of Al(tfacac)<sub>3</sub> given in ref 13.

or Ar ambient. A monomeric derivative appears to be a more probable species than an oligomer since the existence of a monomer is favored by the presence of fluorinated ligands in the metal complex molecule.<sup>3</sup>

The apparent activation energy (24.2 kcal mol<sup>-1</sup>) of the sublimation of Al(tfacac)<sub>3</sub> is in good agreement with the values of the standard enthalpy of sublimation determined by vapor pressure-temperature measurements (Table IV). The value of 9.56 kcal mol<sup>-1</sup> reported for the standard enthalpy of sublimation is probably erroneous because of solubility problems of the vapor phase in the manometric fluid encountered in these experiments.<sup>19,20</sup> The activation energy of the evaporation process of Al(hfacac)<sub>3</sub> of 17.4 kcal mol<sup>-1</sup> is concordant with the standard enthalpy of evaporation of this aluminum complex (Table IV).

**3. Relative Volatility of These Aluminum  $\beta$ -Diketone Chelates.** The volatility of these aluminum  $\beta$ -diketone chelates was found to depend on the vaporization temperature and nature and pressure of the buffer gas. The relative volatility of these compounds cannot be deduced directly from the values of the vaporization rate expressed in mg min<sup>-1</sup> (Figures 4 and 6) since the molar masses of these compounds are very different. A more correct comparison between the volatility of these metal complexes can be established on the basis of data given in Figure 7, where the vaporization rate of these compounds is expressed in mg of aluminum vaporized/min from the boat of 83 mm<sup>2</sup> in cross-sectional area. The vaporization process was considered to occur under 100 Torr of hydrogen or argon (used as a buffer gas) at temperatures ranging from 75 to 175 °C. In addition, these data are valid when the kinetics of vaporization is controlled by the diffusion of the complex molecules in the buffer gas. Actually, from data given in Figure 7, the yield of vaporization can be evaluated in terms of number of Al atoms evolved by vaporization of these aluminum complexes. In the range of temperature investigated, the best yield of vaporization is provided by the sublimation of Al(tfacac)<sub>3</sub> in hydrogen, although this aluminum complex has not the highest saturation vapor pressure (Figure 8).

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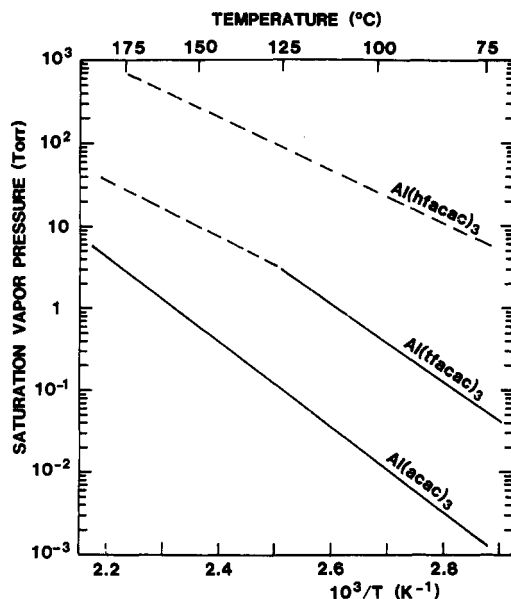
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**Figure 8.** Saturation vapor pressure versus temperature from data given in ref 13 for sublimation (solid line) and evaporation (dashed line) of aluminum(III)  $\beta$ -diketone chelates.

The yields of vaporization corresponding to the sublimation of  $\text{Al}(\text{acac})_3$  in hydrogen, sublimation of  $\text{Al}(\text{tfacac})_3$  in argon, evaporation of  $\text{Al}(\text{hfacac})_3$  in hydrogen at temperatures from 75 to 175 °C, and also the sublimation of  $\text{Al}(\text{acac})_3$  (or more precisely  $\text{Al}_2(\text{acac})_6$ ) in argon between 150 and 175 °C are essentially equivalent. The lowest yields of vaporization are provided by the sublimation of  $\text{Al}(\text{acac})_3$ , i.e.,  $\text{Al}_2(\text{acac})_6$ , in argon below 150 °C, and also by the evaporation of  $\text{Al}(\text{tfacac})_3$  in argon above 125 °C

while the saturation vapor pressure of  $\text{Al}(\text{hfacac})_3$  is higher by a factor of 10 or 100 than that of  $\text{Al}(\text{tfacac})_3$  or  $\text{Al}(\text{hfacac})_3$ , respectively (Figure 8). The data presented in Figures 7 and 8 can serve as a guideline for the selection of the more appropriate volatile precursor to be used in chemical vapor deposition of aluminum containing films.

### Conclusion

The thermogravimetric study of vaporization of aluminum(III)  $\beta$ -diketone chelates such as  $\text{Al}(\text{C}_5\text{H}_7\text{O}_2)_3$ ,  $\text{Al}(\text{C}_5\text{H}_4\text{F}_3\text{O}_2)_3$ , and  $\text{Al}(\text{C}_5\text{HF}_6\text{O}_2)_3$  has demonstrated that the major factors affecting the kinetics of vaporization (in addition to the vaporization temperature) are the nature and pressure of the buffer gas as well as the cross-sectional area of the vaporization boat. The kinetics of the vaporization process was limited by the diffusion of these large complex molecules in the buffer gas from the boat to the cold wall of the thermogravimetric analyzer. The apparent activation energy of sublimation of aluminum(III) acetylacetonate was dependent on the nature of the buffer gas, suggesting that dimer  $\text{Al}_2(\text{acac})_6$  or monomer  $\text{Al}(\text{acac})_3$  molecules may be evolved by sublimation of the compound in argon or hydrogen, respectively. The values of the activation energy of these vaporization processes were in relatively good concordance with those of the standard enthalpy of sublimation or evaporation reported in the literature and determined by other techniques. The experimental data expressed in terms of number of aluminum atoms provided by vaporization of these metal complexes in combination with the data of saturation vapor pressure can help for the selection of the more appropriate precursor to be used in CVD of aluminum-containing films.

**Registry No.**  $\text{Al}(\text{C}_5\text{H}_4\text{F}_3\text{O}_2)_3$ , 14354-59-7;  $\text{Al}(\text{C}_5\text{HF}_6\text{O}_2)_3$ , 15306-18-0;  $\text{Al}(\text{C}_5\text{H}_7\text{O}_2)_3$ , 13963-57-0.

## Mechanistic Studies of the Conversion of Borazine Polymers to Boron Nitride

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The thermal chemistry of thin films of a borazinylamine polymer deposited on KOH-etched aluminum and sapphire has been examined by thermal decomposition mass spectroscopy, thermogravimetric analysis, and Raman spectroscopy. The majority of the gas evolution chemistry is found to occur below 400 °C. All products desorb with the same temperature profile, and the major desorbing species are  $\text{NH}_3$  and  $\text{N}_2$  (polymer decomposition products) and  $\text{HCl}$  (side reaction products). The hydrogen remaining in the solid at 400 °C ( $\approx 50\%$ ) is continuously lost from 400 to 1200 °C. Facile ring-opening steps are evidenced by the complete isotope mixing that occurs for samples in which the ring nitrogens are labeled with  $^{15}\text{N}$ . With increasing pyrolysis temperature, the Raman spectra change from that characteristic of the polymer (25 °C) to an intense featureless fluorescence spectrum (up to 400 °C), to an intense three-peak resonance Raman spectrum ( $\approx 400$  to 1200 °C), and finally to a less intense Raman spectrum characteristic of h-BN superimposed on a fluorescence background at 1600 °C. The implications of these observations to the pyrolysis mechanism are discussed.

### Introduction

Soluble or fusible inorganic polymers offer several benefits for the formation of ceramic materials, and they furnish reagents with which to probe the mechanistic aspects of ceramic formation. In addition, polymers provide

access to ceramic forms such as fibers, foams, and some coatings not available from classical ceramic processing.<sup>1-3</sup>

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