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Determination of the enthalpies of sublimation and evaporation from thermogravimetric data: Application to metalorganic complexes of Al and Cr

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ABSTRACT

A series of bimetallic acetylacetonate (acac) complexes, $Al_xCr_{1-x}(acac)_3$, $0 \le x \le 1$, have been synthesized for application as precursors for the CVD of substituted oxides, such as $(Al_xCr_{1-x})_2O_3$. Detailed thermal analysis has been carried out on these complexes, which are solids that begin subliming at low temperatures, followed by melting, and evaporation from the melt. By applying the Langmuir equation to differential thermogravimetry data, the vapour pressure of these complexes is estimated. From these vapour pressure data, the distinctly different enthalpies of sublimation and evaporation are calculated, using the Clausius–Clapeyron equation. Such a determination of both the enthalpies of sublimation and evaporation of complexes, which sublime and melt congruently, does not appear to have been reported in the literature to date.

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1. Introduction

The application of metal β-diketonates as precursors for metalorganic chemical vapour deposition (MOCVD) has been studied for various metal oxides [1–3]. These metal β-diketonates (such as acetylacetonates, denoted as ‘acac’) are often sufficiently volatile, relatively easy to synthesise and purify, and non-toxic. They do not in general decompose during the transport of precursor from vapouriser to the reaction zone of the CVD chamber, usually maintained at an elevated temperature. They have a reasonably long shelf life. These properties make them suitable as MOCVD precursors. Requirement for thin films of complex oxides, such as dielectrics and high-T_c superconductors, has prompted interest in the development of suitable chemical precursors to them. The use of metal β-diketonate precursors, one for each metal in an oxide, for depositing a film of multi-metal oxides has already been established. An alternate approach is to synthesize complexes with more than one metal in them, the so-called single-source precursors, to deposit thin films of a substituted metal oxide such as $(Al_{1-x}Cr_x)_2O_3$ [4].

Thermal properties of metal complexes intended for use as CVD precursors need to be studied in detail, for they are often subliming solids. Such a study is especially important for single-source precursors, to ensure that they do not decompose upon vapourisation, and that the composition of the vapour is the same as that of the complex. This, in turn, helps control the composition of the film being grown using a given complex. Further, it is desirable to measure the vapour pressure of the complex, so that the precursor flux during a CVD process may be quantified and controlled.

Even so, vapour pressure data for metal complexes employed as precursors used in the CVD of various metal oxides are not generally available in the literature, while vapour pressure values for various organic compounds have been reported [5]. Vapour pressure determination may be done conveniently using thermogravimetric analysis (TGA), employing the Langmuir equation [6]. For example, to estimate the limits on the inhalation of the vapours emitted by drugs and dyes, the vapour pressure dependence on temperature has been studied [6,7]. Using this method, Chatterjee et al. have published a detailed study of the vapour pressure of single component systems [7]. For systems to obey the Langmuir equation, it is a requisite that the vapourisation process follows zero order kinetics. Sublimation and evaporation are generally zero order processes, though there are exceptions to this. For example, multi-step decomposition concomitant with the evaporation process is not of zero order [8].

Recently, a modified and a better-founded approach to the Langmuir equation was reported, wherein the mass diffusion of the subliming substance due to the flowing gas in the TGA apparatus was taken into account. This has been shown to be necessary because the Langmuir equation is strictly valid only for vapourisation into absolute vacuum [9]. Nevertheless, the validity in practice

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of using the Langmuir equation has been established by showing that the vapour pressure estimated by using the Langmuir equation matches closely with that measured by the Knudsen method under appropriate conditions, such as low heating rates and the choice of a suitable standard [6].

The acetylacetonates of Al and Cr are known to sublime, and have been used as precursors to the CVD of Al_2O_3 and Cr_2O_3, respectively [10]. A similar thermal behaviour might be expected of the substituted complexes, $Al_xCr_{1-x}(acac)_3$ ($0 < x < 1$). In this paper, we report the synthesis of these substituted (bimetallic) complexes intended for use as precursors for the MOCVD of $(Al_xCr_{1-x})_2O_3$ thin films, and the estimation of their vapour pressure from thermogravimetric data. The estimation of the enthalpy of vapourisation from the vapour pressure data leads to distinct values for the enthalpy of sublimation and the enthalpy of evaporation from the melt of these complexes, in which both the initial sublimation and subsequent evaporation from the melt occur congruently.

2. Experimental

$Al(acac)_3$ and $Cr(acac)_3$ were synthesized as reported in literature [11]. The substituted complexes, $Al_xCr_{1-x}(acac)_3$ ($0 < x < 1$), were prepared by a co-synthesis strategy, wherein appropriate amounts of $Al_2(SO_4)_3{\cdot}16H_2O$ and $CrCl_3{\cdot}6H_2O$ were dissolved in water, followed by the addition of the acetylacetone ligand. The resulting solution was neutralized using 1:1::NH_3:H_2O, to give a precipitate of $Al_xCr_{1-x}(acac)_3$. The crude was recrystallized using acetone. The complexes, crystalline solids that begin to sublime at about 160 °C, were characterized by mass spectrometry, IR spectroscopy, and elemental analysis. The metal composition of the substituted complexes was determined by fixing the occupancy of the metal sites using single-crystal X-ray diffraction data. The two specific compositions of the substituted complex on which measurements are reported here, $Al_{0.78}Cr_{0.22}(acac)_3$ and $Al_{0.90}Cr_{0.10}(acac)_3$, will henceforth be referred to as AlCr1 and AlCr2, respectively.

Thermal analysis was carried out on a TA Instruments SDT Q600 simultaneous TG/DTA (thermogravimetric/differential thermal analyzer). All thermogravimetric (TG) experiments were repeated at least thrice to confirm reproducibility of the data. About 20 mg of each sample was taken in a platinum crucible (90 µl). Alumina was used as the reference. Ultra-high purity nitrogen gas, at a flow rate of 100 ml/min, was used for the TG experiments. A heating rate of 10 °C/min was used for all the measurements. From these data, vapour pressure as a function of temperature was deduced for $Al(acac)_3$, $Cr(acac)_3$, $Al_{0.78}Cr_{0.22}(acac)_3$ and $Al_{0.90}Cr_{0.10}(acac)_3$, using the Langmuir equation [12]:

$$P = \left[\left(\frac{dm}{dt}\right)\sqrt{\frac{T}{M}}\right]\left[\frac{\sqrt{2\pi R}}{\alpha 1}\right] \tag{1}$$

where P is the vapour pressure at temperature T, dm/dt is the rate of weight loss per unit surface area during the TG experiment, M is the molecular mass of the material, R is the gas constant, and α_1 is the vapourisation coefficient. In vacuum, α_1 is assumed equal to 1, but in the flowing gas environment of the TG experiment, α_1 is significantly different, and has to be determined experimentally. The term $\left[\sqrt{2\pi R}/\alpha_1\right]$, which is dependent on the instrument and the experimental conditions, is often referred to as 'k' in the literature. The value of 'k' was calculated using benzoic acid (Analytical Reagent grade) as the standard. The vapour pressure data for benzoic acid were taken from literature [13]. Benzoic acid was used as the standard because the range of temperatures over which it vapourises is the same as that for the acetylacetonate complexes studied by us [9,6].

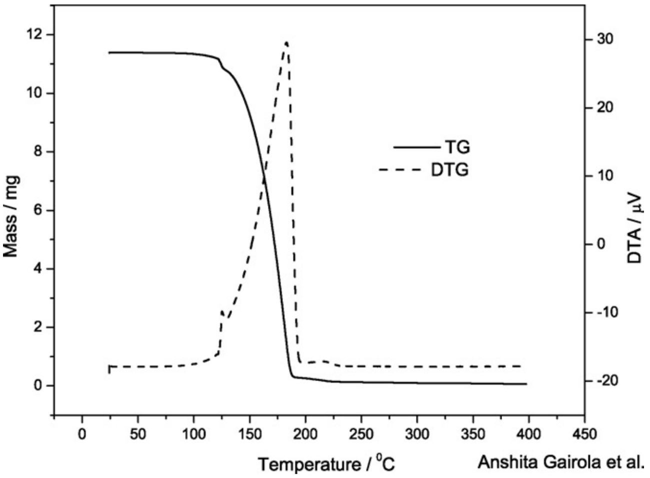

Fig. 1. TG/DTG plot of benzoic acid.

From these vapour pressure data, the values of enthalpy of sublimation and evaporation were computed, using the Clausius–Clapeyron equation:

$$\ln P = A - \frac{\Delta H}{RT} \tag{2}$$

3. Results and discussion

The TG data for benzoic acid, and the differential thermogravimetry (DTG) data derived from it, are plotted in Fig. 1. The vapour pressure–temperature data for benzoic acid were deduced from the Antoine constants in the relevant temperature range taken from literature [13]. Using these data and the mass derivative with respect to time obtained from the DTG plot, the value of k was calculated using Eq. (1). The value of k was found to be 90,606 $J^{1/2}\,K^{-1/2}\,mol^{-1/2}$, which is in substantial agreement with the value of $\sim 10^5$ reported by Wright et al. [8]. This value of 'k' was used for all further calculations.

The thermal behaviour of the complexes $Al(acac)_3$ and $Cr(acac)_3$ has been reported in literature [12], showing that both of these complexes undergo a single-step weight loss, without decomposing in the process. The complex $Cr(acac)_3$ has a higher melting point, and has a lower volatility (at a given temperature) than $Al(acac)_3$. Fig. 2 shows the characteristic plot of the TG/DTG/DTA data for the complex AlCr1 synthesized in this work. Fig. 3 shows the overlay of the TGA data of all the four complexes, pure and substituted. The TGA

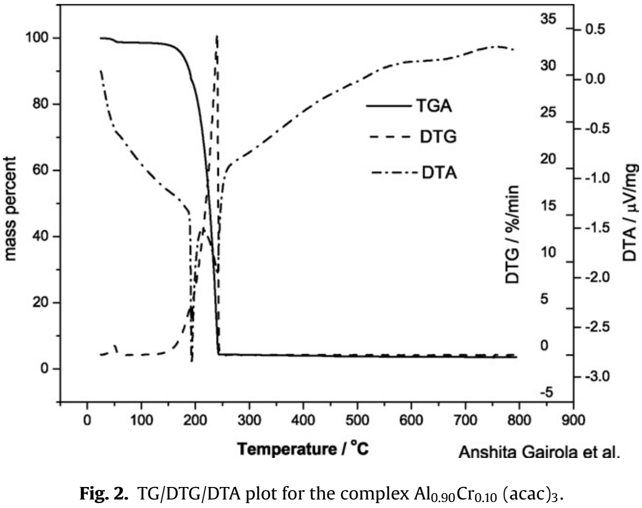

Fig. 2. TG/DTG/DTA plot for the complex $Al_{0.90}Cr_{0.10}$ $(acac)_3$.

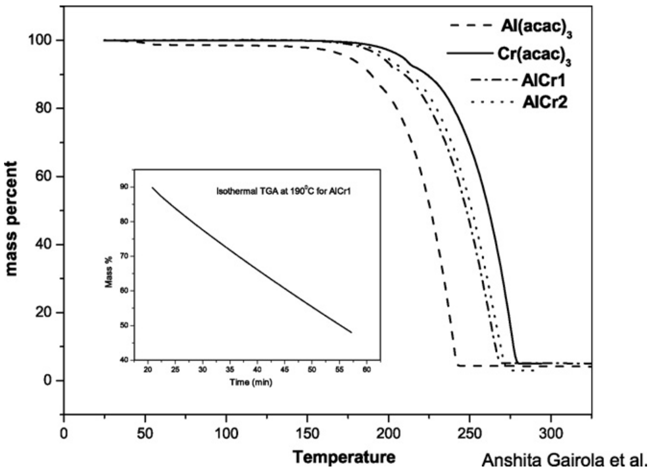

Fig. 3. Overlay of TGA plots of the four complexes, showing that volatility decreases as the Cr content of the complex increases. Inset shows isothermal TGA for AlCr(acac)$_3$.

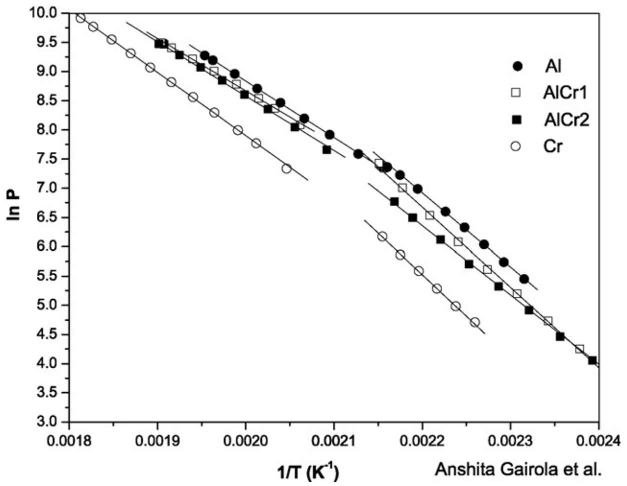

Fig. 4. Plot of ln P vs. $1/T$ for the four complexes, showing distinct slopes for the sublimation regime and the regime of evaporation from the melt.

of AlCr1 shows a single-step weight loss, implying that the complex does not decompose, even as it vapourises completely, leaving no residue. A similar thermal behaviour is also observed in the complex AlCr2. That is, the thermal behaviour of the substituted complexes is analogous to that of the complexes Al(acac)$_3$ and Cr(acac)$_3$, their melting points and volatility having values intermediate to those of the "end members", *viz.*, Al(acac)$_3$ and Cr(acac)$_3$, as seen in Fig. 3.

The DTG graph in Fig. 2 shows a monotonic rise, followed by a sharp fall after the complete loss of mass of the complex AlCr1 from the crucible, indicating that the process involved is of zero order. A similar behaviour has been recorded for all the four compositions studied here. The zero order behaviour ensures that vapour pressure of the complexes may be deduced from thermogravimetric data [7]. This is further supported by the isothermal TGA, shown in the inset in Fig. 3. The isothermal plot of weight loss at 160 °C as a function of time is seen to be linear. These observations confirm that the sublimation process in question is of zero order [14]. The DTA curve in Fig. 2 shows two peaks: the first peak corresponds to the melting, while the second corresponds to evaporation from the melt.

From Fig. 3, it can be seen that the weight loss steps of the two bimetallic complexes lie in between those of the pure complexes, Al(acac)$_3$ and Cr(acac)$_3$. As already noted, Al(acac)$_3$ has a weight loss step at a lower temperature than does Cr(acac)$_3$. The weight loss steps show a shift towards a higher temperature as the percentage of chromium in the complex is increased. The complex AlCr2 has higher chromium content than AlCr1 does and hence the weight loss step for AlCr2 lies at a higher temperature than for AlCr1.

The vapour pressure of each complex, deduced from the TGA data, is plotted as ln P vs. $1/T$ in Fig. 4. It is seen that, as the chromium content of the complex increases, the vapour pressure at a given temperature decreases. Specifically, pure Cr(acac)$_3$ has a lower vapour pressure than pure Al(acac)$_3$, at any given temperature. Using the Clausius–Clapeyron equation, the slope of the resulting straight line gives $\Delta H/R$ and, thus, the enthalpy ΔH of the process taking place. It is to be noted from the TGA data (Fig. 2) that weight loss in the complexes begins at a temperature significantly lower than the melting point (MP), as observed in DTA (Fig. 2), and ends at a temperature higher than the MP. Thus, below the MP, the (deduced) vapour pressure of the complex is due to sublimation. Beyond the melting point, the vapour pressure is due to evaporation from the molten complex (liquid). That both the sublimation and melting processes of the substituted complexes are congruent was verified as follows. The FTIR spectrum and the elemental analysis (C, H, and N analysis) were obtained for each complex as prepared. These were compared with the corresponding data for a sample of the complex from which sublimation was carried out at a temperature lower than the melting point. The FTIR spectrum and the elemental composition of the complex before and after sublimation were found to be identical, establishing that congruent sublimation takes place below the MP of the complex. Similarly, the FTIR spectra and the elemental composition of the as-prepared complex were compared to those of the complex taken to a temperature (just) above the MP. The identity of the corresponding data established that the complexes melt congruently.

As the sublimation and evaporation processes occur congruently, and as the intermolecular binding forces in the solid and molten states of the complex can be different, the enthalpies of sublimation and evaporation from the melt are expected to be different. This is indeed so, as evident from the need to fit the data above and below the melting point to two different straight lines. Specifically, as intermolecular bonding is stronger in solids than in liquids, the enthalpy of sublimation, which involves the transition from solid to gaseous phase, is expected to require more energy than evaporation, which involves the transition from the liquid to the vapour state. Thus, the enthalpy of sublimation may be expected to be greater than the enthalpy of evaporation from the melt. This expectation is verified, as shown by the data in Table 1, wherein the enthalpies of sublimation and evaporation from the melt (ΔH_{sub} and ΔH_{eva}) of each of the complexes studied here are listed, together with their melting points obtained from the DTA data. It is to be noted that the values of ΔH_{eva} for Al(acac)$_3$ and Cr(acac)$_3$ match very well with the values obtained by the Knudsen method [15].

While differing values of ΔH_{sub} and ΔH_{eva} are to be expected when sublimation and evaporation are both congruent for a given compound, such distinct enthalpies do not appear to have been reported previously. Wright et al. [8] have calculated the vapour pressure and enthalpy of triethanolamine, a compound that

Table 1
Enthalpies of sublimation and evaporation of the four complexes, together with their melting points.

Complex	at.% of Cr	Melting point	ΔH_{sub} (kJ/mol)	ΔH_{eva} (kJ/mol)
Al(acac)$_3$	Pure	193 °C	107.1	80.2
AlCr1	10%	195 °C	109.9	74.3
AlCr2	22%	201 °C	98.2	75.6
Cr(acac)$_3$	Pure	213 °C	120.8	89.9

sublimes before it undergoes melting, followed by evaporation from the melt. However, the distinction between the enthalpies of sublimation and evaporation from the melt seems to have been missed in this case, as the slopes of the two segments of the linear fit to $\ln P$ vs. $1/T$ (*i.e.*, ΔH_{sub} and ΔH_{eva}) are nearly the same.

4. Conclusions

Using thermogravimetric analysis and the Langmuir equation, the vapour pressure of four metalorganic complexes of the form $\mathrm{Al}_x\mathrm{Cr}_{1-x}(\mathrm{acac})_3$ have been determined as a function of temperature. From these vapour pressure data, and using the Clausius–Clapeyron equation, the distinct enthalpies for congruent sublimation, and for congruent evaporation from the melt, ΔH_{sub} and ΔH_{eva}, have been calculated. The value of ΔH_{sub} is higher than ΔH_{eva}, as might be expected. The ΔH values determined from the thermogravimetry data are in very good agreement with those determined by the effusion technique. Even though the Langmuir equation is strictly valid for vapourisation into vacuum, the close agreement found here is attributable to the choice of benzoic acid as the standard. Thus, provided an appropriate standard is chosen, thermogravimetry carried out at a finite pressure, under gas flow, might be used to determine the vapour pressure of subliming solids often used as CVD precursors, thereby simplifying the quantitative design of CVD processes.

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