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Sublimation kinetics of scandium *β*-diketonates

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Abstract The volatile scandium-*β*-diketonates are synthesised using acetylacetone (acac) and tetramethylheptanedione (tmhd) as coordinative ligands for CVD application. The X-ray powder patterns are indexed and analysed and found to be orthorhombic and monoclinic phases for $Sc(acac)_3$(1) and $Sc(tmhd)_3$(2) respectively. The sublimation and evaporation kinetics have been analyzed using three calculating techniques. The non-isothermal based activation energy values are found to be 38 ± 2 and 73 ± 2 kJ mol^{-1} by Flynn–Wall technique for (1) and (2) respectively. The measured E_a values are close to the value obtained using Kissinger method.

Keywords Powder X-ray diffraction · Scandium-*β*-diketonate · Sublimation kinetics

Introduction

Metal *β*-diketonate complexes that are of particular relevance to this paper have been used as highly volatile precursors for chemical vapor deposition of films with novel multifunctionalities and a wide variety of applications in modern high technology, including semiconductor microelectronics, damage resistance, antireflection, and high-reflection multilayer coatings in light emitting diodes and high power pulsed solid state UV-lasers, ferroelectric, dielectric, protective layers and catalysis. The precursors need to be designed in such a way that the compounds are volatile and thermally stable at growth temperatures [1, 2]. The volatility and thermal stability of *β*-diketonate of metals in different oxidation states have been reported [3]. However, the studies on sublimation kinetics of Sc-*β*-diketonate have not been reported. TG has been used to obtain the thermal decomposition parameters of solid chemicals [4]. These approaches are based on monitoring weight change as an indicator of solid-state conversion and may be performed under isothermal, non-isothermal, or modulated conditions [5, 6]. The data generated from these experiments can be analyzed and manipulated by either model [7] or model-free [8] approaches to obtain Arrhenius kinetic parameters such as activation energy (E_a) and pre-exponential factor [9].

The present study was carried out for the sublimation kinetics [10] of volatile tris(2,4-pentanedionato)scandium(III) ($Sc(acac)_3$) and tris(2,2,6,6-tetramethyl-3,5-heptanedionato)scandium(III) ($Sc(tmhd)_3$) by means of thermal analysis (TG and DTG).

Experimental section

Materials

Crystalline scandium-*β*-diketonates are obtained from the reaction of scandium nitrate with corresponding equivalents of 2,4-pentanedione or 2,2,6,6-tetramethyl-3,5-heptanedione in basic medium [11].

Instrumentation

The ^1H and ^{13}C NMR spectra of the scandium-*β*-diketonates solutions were recorded with a Bruker spectrometer.

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Melting points were obtained in a sealed capillary using optical microscopy. To determine the thermal behavior of the complexes besides the congruent nature of vaporization to nil residues under reduced pressure (2 mbar), vapor or mass transport study under vacuum was carried out. The experimental conditions are the same as described earlier [12]. Mass spectra of the samples were recorded with a Micromass LCT time-of-flight mass spectrometer operating in electron spray mode. The X-ray diffraction analyses of the complexes were carried out using an upgraded Philips PW-1730 X-ray diffraction system interfaced with VisXRD software. Horizontal Perkin-Elmer Pyris-Diamond TG-DTA thermal analyzer was adopted for non-isothermal and isothermal analyses. The measurement was carried out in platinum crucible under high pure nitrogen, which was dried by passing through molecular sieves (Linde 4A) with a flow rate of 12 dm^3 h^{-1} at a linear heating rate of 10 K min^{-1} in ambient pressure. Non-isothermal TG measurements are run at 4, 6, 8 and 10 K min^{-1} with a sample size of 1–6 mg to provide a control set of values for thermal sublimation parameters. The experimental conditions are the same as described earlier [13, 14]. Prior to the isothermal measurements, blank runs were carried out with a flow rate of 20 dm^3 h^{-1} of dry nitrogen gas, from room temperature to 1173 K at a heating rate of 10 K min^{-1} keeping the reference and sample pans empty. The system was then cooled to ambient temperature under the same conditions. The powdered sample was spread out on a platinum crucible and was flushed with nitrogen at a rate of 6 dm^3 h^{-1} at ambient temperature. The initial heating to ~360 K, is rather rapid (10 K min^{-1}), and after temperature stabilisation, the sample is subsequently heated (2 K min^{-1}) in steps of 10 K to isothermal temperatures in the range 376–407 K and 385–475 K for (1) and (2), respectively.

Kinetic procedure

Solid state decomposition kinetics is usually described by the following basic equation:

$$\frac{da}{dt} = k(T)f(\alpha) \tag{1}$$

where α is the degree of reaction defined as $\alpha = (w_i - w_T)/(w_i - w_f)$ (being w_i and w_f the initial and final mass loss, while w_T is the mass loss at temperature T), $f(\alpha)$ is the model function, which assumes different mathematical forms depending on the reaction mechanism [15] and $k(T)$ is the specific rate constant, whose temperature dependence is commonly described by the Arrhenius equation [16]:

$$lnk(T) = \ln A - E_a/RT \tag{2}$$

where E is the activation energy, A is the preexponential factor, R the gas constant and T the absolute temperature. The plot of ln k versus 1/T is linear and from the slope, the activation energy (E_a) for the sublimation of the complex was calculated.

The proposed kinetic analysis, based on dynamic model-free methods using data obtained at different fixed heating rates, β, seems to be the most reliable approach. The thermal sublimation kinetics is examined using Kissinger Technique [17–19]:

$$\ln\frac{\beta}{T_m^2} = \ln\left(\frac{AR\left(n(1-\alpha)_m^{n-1}\right)}{E_a}\right) - \frac{E_a}{RT_m} \tag{3}$$

where T_m is the DTG peak temperature at a given β value, A the pre-exponential factor, E_a the activation energy and R the gas constant. The E_a value can be calculated from the slope of ln (β/T_m^2) as a function of $1/T_m$.

Kinetic study of sublimation steps was also performed using the isoconversional method of Flynn–Wall Technique [20]. The isoconversional expression is,

$$ln\beta = \ln\left(\frac{AE}{R}\right) - \ln[F(\alpha)] - \frac{E_a}{RT} \tag{4}$$

The activation energy, E_a can be calculated from a plot of ln β versus $1/T$ at a fixed weight loss since the slope of such a line is given by E_a/R (gas constant 8.314 J mol^{-1} K^{-1}). The ln A is calculated from the intercept value of the line and the derived E_a value.

For isothermal TG measurements at several isothermal temperatures [21]:

$$ln\left(\frac{d\alpha}{dt}\right)m = lnA + n\ln(1-\alpha_m) - E_a/RT \tag{5}$$

The E_a value of isothermal degradation was calculated from the slope of the plot of the maximum weight-loss rate, $\ln(d\alpha/dt)_m$ versus the reciprocals of the several isothermal temperatures.

Results and discussion

The scandium-β-diketonates are systematically characterised by ^{1}H NMR and Mass Spectral studies. ^{1}H and ^{13}C NMR (298 K, 300 MHz, $CDCl_3$, δH, ppm) of $Sc(acac)_3$(1): 1.997 (s, 6H, $^\bullet CH_3$), 5.505–5.552 (s, 1H, =CH); ^{13}C NMR (298 K, 75 MHz, $CDCl_3$, δ, ppm): 26.84–27.12 ($^\bullet CH_3$), 103.32 (=CH) and 191.82 ($^\bullet C{=}O$). ES-MS: m/z = 342 and 243 in the spectrum are due to the fragmentation of $[Sc(acac)_3]^+$ and $[Sc(acac)_2]^+$ from the molecular mass (343). $Sc(tmhd)_3$(2) demonstrates the following: ^{1}H NMR (298 K, 300 MHz, $CDCl_3$, δH, ppm): 0.915, 1.206, 1.337

(s, 6H, $^{\bullet}CH_3$), 5.800 (s, 1H, =CH); ^{13}C NMR (298 K, 75 MHz, $CDCl_3$, δ, ppm): 28.07 ($^{\bullet}CH_3$), 40.38(C–CH_3), 92.04 (=CH), and 200.89 ($^{\bullet}$C=O). NMR chemical shifts [22] are close to those observed for olefinic protons, and they are independent of the size, charge, and $^{\bullet}$-bonding ability of the metal ion. Holm and Cotton [23] had earlier examined the –CH = resonances of several neutral metal acetylacetonates in carbon tetrachloride solution. The melting and sublimation/vaporization to nil residues for $Sc(acac)_3$ and $Sc(tmhd)_3$ under reduced pressure were carried out to demonstrate the clean volatilisation behaviour. The observed melting points from this study (at $\sim$2 mbar) were 453 and 417 K for $Sc(acac)_3$ and $Sc(tmhd)_3$, respectively. The sublimed product was found to have the same XRD and IR as the initial product taken. ES-MS: m/z values 594, 537, 411, 185 and 127 corresponds to $[Sc(tmhd)_3]^+$, $[Sc(tmhd)_3\text{-}C_4H_9]^+$, $[Sc(tmhd)_2]^+$, $(tmhd)^+$ and $[(tmhd)\text{–}C_4H_8]^+$. The powder X-ray diffraction patterns of $Sc(acac)_3$ and $Sc(tmhd)_3$ were recorded in 2θ range of 5° to 70°, measured in steps and speed of 0.02° and 2° min^{-1} respectively. The powder diffraction pattern is indexed by the programme DICVOL04 technique in FullProf package [24]. The full pattern fitting, peak decomposition and space groups are performed using the program chekcell in CRYSFIRE package. The profile is fitted using the pseudo-Voigt function [25]. The X-ray data analysis of crystalline powder (1) gave: a = 16.79 Å, b = 15.47 Å; c = 13.71 Å, $\alpha = \beta = \gamma = 90°$, V = 3560.42 Å^3, space group = Pbca, crystal system: orthorhombic which are in agreement with the single crystal data [26]. The results revealed the crystalline nature and phase purity of the compound. The powder pattern of (2) gave: a = 24.44 Å, b = 18.34 Å, c = 17.59 Å, $\alpha = \gamma = 90°$, $\beta = 96.34°$, V = 7839.76 Å^3, space group = $P2_1$, crystal system = monoclinic which agreed with the single crystal data [27].

Non-isothermal kinetics

A strong and regular effect of the heating rate on the non-isothermal TG curves of the $Sc(acac)_3$ and $Sc(tmhd)_3$ are shown in Fig. 1. The volatilization processes are a single-step process in the defined temperatures ranges. The sublimation temperature rises with the increasing of the heating rate. Figure 2 shows that the heating rates effect on the temperatures at the maximum weight-loss rate (T_p), at the beginning (T_o) and at the end (T_f) of the weight-loss of $Sc(acac)_3$ and $Sc(tmhd)_3$ TG, respectively. It is found that the values of T_p, T_o and T_f increases of heating rates. Linear fittings of T_o, T_p and T_f versus β/K min^{-1} gives Eq. 6–8, respectively.

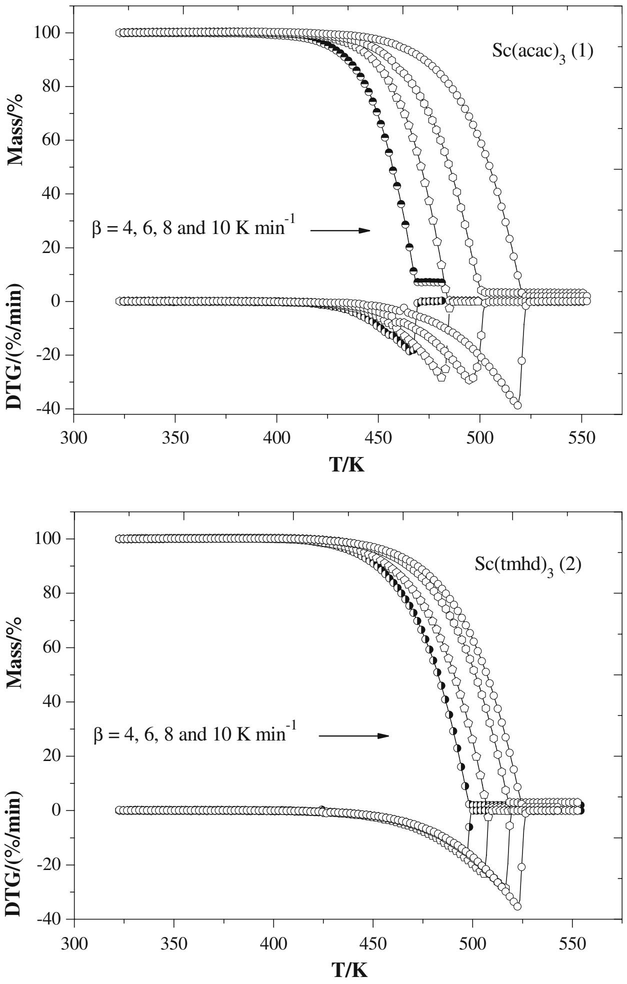

Fig. 1 The effect of the heating rate on the TG curves of the $Sc(acac)_3$ (1) and $Sc(tmhd)_3$ (2)

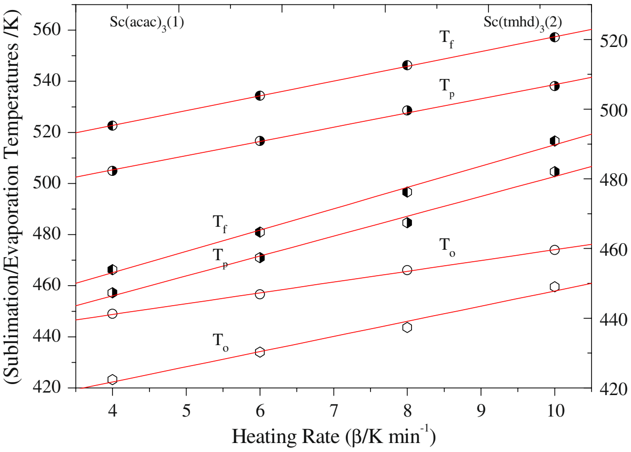

Fig. 2 Plots of the sublimation temperatures versus heating rates

Table 1 The sublimation kinetics of the $Sc(acac)_3$ and $Sc(tmhd)_3$ by various methods

Non-isothermal process				Isothermal process		
Compound	Kissinger	Flynn–Wall		Arrhenius Plot		
	Ea/kJ mol^{-1}	α	Ea/kJ mol^{-1}	β/Km in^{-}	^{1} Ea/kJ mol^{-1}	Ea/kJ mol^{-1}
1	38 ± 2	0.1	42 ± 3	4	114^{a}	81 ± 2 (375–450 K)^{a}
		0.2	40 ± 2		82^{b}	
		0.3	38 ± 2	6	117^{a}	
		0.4	37 ± 2		81^{b}	
		0.5	37 ± 2	8	112^{a}	
		0.6	37 ± 1		78^{b}	
		0.7	36 ± 2	10	83^{b}	
		0.8	36 ± 2			
	38 ± 2		38 ± 2			
2	67 ± 5	0.1	71 ± 3	4	80^{b}	95 ± 3 (356–414 K)^{a}
		0.2	78 ± 5	6	79^{b}	75 ± 3 (434–465 K)^{b}
		0.3	76 ± 6	8	79^{b}	
		0.4	74 ± 7	10	78^{b}	
		0.5	73 ± 6			
		0.6	72 ± 6			
		0.7	73 ± 6			
		0.8	72 ± 8			
	67 ± 5		73 ± 6			

α conversion; β heating rate

[a] Sublimation process

[b] vaporisation process

$$Sc(acac)_3(1) \quad Sc(tmhd)_3(2)$$

$$\begin{aligned} T_o &= 5.9\beta/\mathrm{K\,min^{-1}} + 398\,\mathrm{K}; \\ T_o &= 3.1\beta/\mathrm{K\,min^{-1}} + 428\,\mathrm{K} \end{aligned} \tag{6}$$

$$\begin{aligned} T_p &= 7.7\beta/\mathrm{K\ min^{-1}} + 424\mathrm{K}; \\ T_p &= 4.1\beta/\mathrm{K\ min^{-1}} + 466\mathrm{K} \end{aligned} \tag{7}$$

$$\begin{aligned} T_f &= 8.3\beta/\mathrm{K\,min^{-1}} + 431\,\mathrm{K}; \\ T_f &= 4.2\beta/\mathrm{K\,min^{-1}} + 478\,\mathrm{K} \end{aligned} \tag{8}$$

The equilibrium sublimation temperatures are gained by extrapolation of T_o, T_p and T_f to $\beta = 0$: $T_o^o = 398, 428$ K, $T_p^o = 424, 466$ K and $T_f^o = 431, 478$ K for (1) and (2), respectively.

According to the equations of Kissinger and Flynn–Wall techniques the activation energy of sublimation for (1) and (2) are measured (Table 1). Using Kissinger method, Eq. 3, the activation energy can be calculated from the plot of $\ln(\beta/T_m^2)$ versus $1000/T_m$ (Fig. 3). The obtained activation energy values are 38 ± 2 and 67 ± 5 kJ mol^{-1} for (1) and (2), respectively. The activation energy can also be determined using the method Flynn–Wall technique, from the linear fitting of ln β versus 1/T at different conversions values, which is from 0.1 to 0.8 (Fig. 4). Figure 3 shows that the lines are nearly parallel, indicating the applicability of this method to our metallorganic complexes system in the conversion range studied. This fact suggests that a single reaction mechanism is operative. Mean values of 38 ± 2 kJ mol^{-1} and 73 ± 6 kJ mol^{-1} are found for (1) and (2), respectively. Table 1 shows that the activation energy is very close to the value obtained using Kissinger method. Compared to other methods these two methods

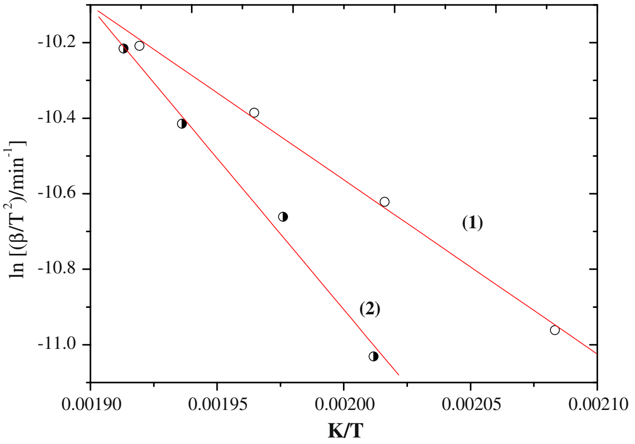

Fig. 3 Plots of $\ln[(\beta/T^2)/\mathrm{min}^{-1}]$ versus 1/T at different heating rates according to Kissinger method

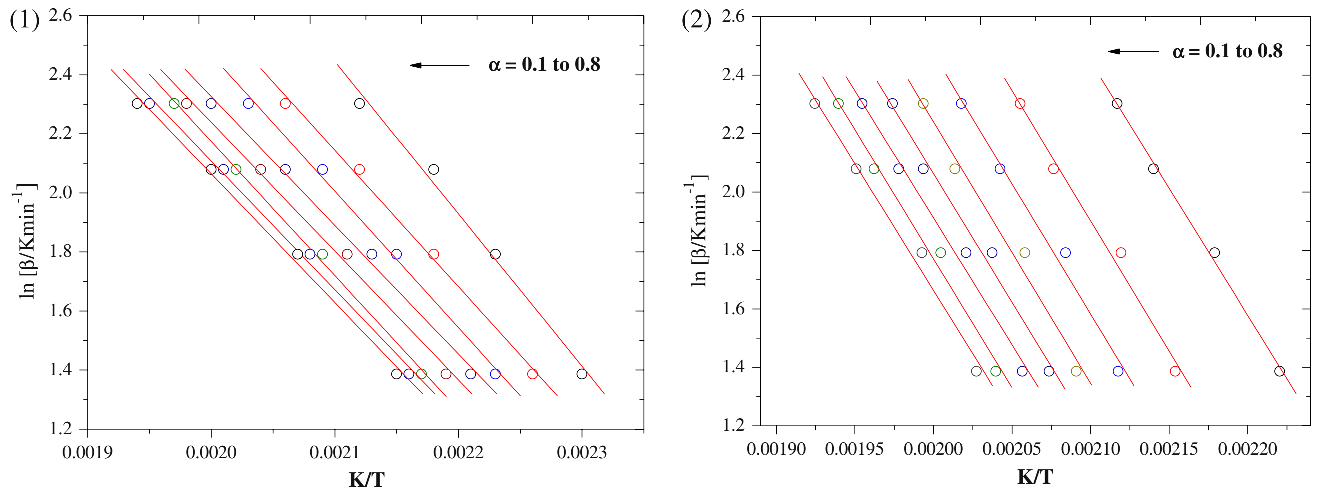

Fig. 4 Plots of ln [β/K min^{-1}] against 1/T with weight loss from 0.1 to 0.8 in steps of 0.1 according to Flynn–Wall method (β = 4, 6, 8 and 10 K min^{-1}) for (1) and (2)

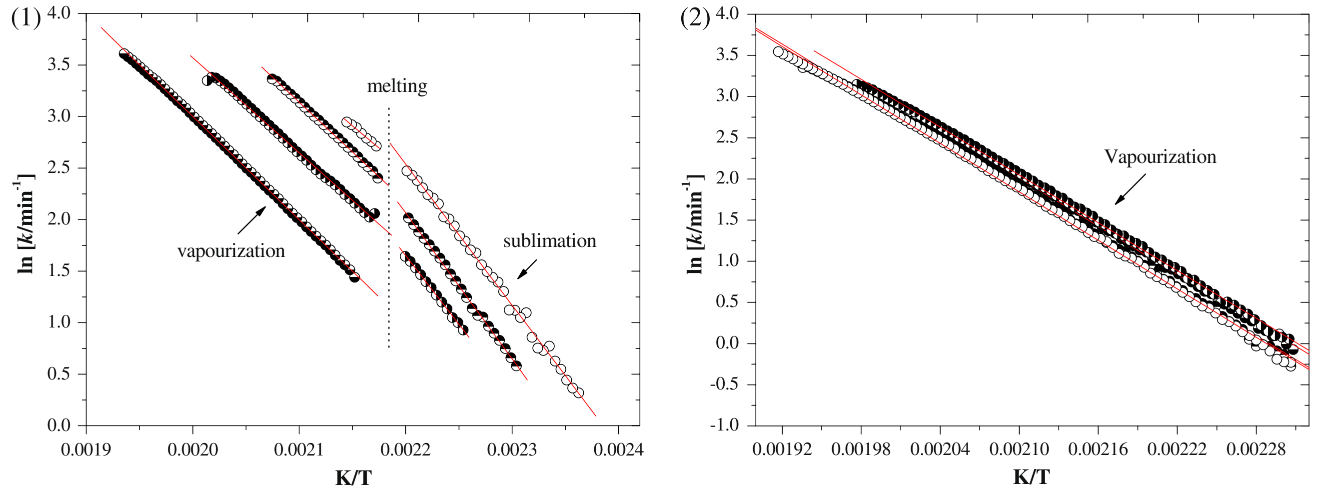

Fig. 5 Plots of ln [k/min^{-1}] against 1/T with weight loss from 5% to 90% according to Arrhenius plots (β = 4, 6, 8 and 10) for (1) and (2)

present the advantage that they do not require previous knowledge of the reaction mechanism for determining the activation energy [28, 29].

Further, the activation energy values of Sc precursors were derived from the plot of ln k versus 1/T (Arrhenius plot). The expression for k is given by $k = d\alpha/dt$, where $d\alpha/dt$ is the derivative of the fraction sublimation with respective to time and k the rate of sublimation. It should be noted from TG curves given in Fig. 1 that sample mass loss at the temperature region below the melting point (i.e. below 457 K) is due to Sc(acac)$_3$(1) sublimation (e.g. sample mass loss at the melting point equals ~40% at 4 K min^{-1} heating rate, while at 10 K min^{-1} heating rate sample mass loss at the melting points equals ~5%), while mass at the temperature region above the melting point is due to Sc(acac)$_3$(1) evaporation process. Thus, the kinetic parameters were evaluated for different degrees of conversions, taking in mind that data points for the temperature region below melting point corresponding to sublimation, while data points for the temperature region above the melting point corresponding to evaporation (Table 1). Over this range of conversion, Arrhenius plots of ln k versus 1/T (Fig. 5) is a linear plot from which vaporisation activation energy (Ea) can be calculated as 82, 81, 78 and 83 kJ mol^{-1} for the heating rate of 4, 6, 8 and 10 K min^{-1}, respectively, for Sc(acac)$_3$. The activation energy values with respect the heating rates of 4, 6, 8 and 10 K min^{-1} are found to be 80, 79, 79 and 78 kJ mol^{-1}, respectively for evaporation process of Sc(tmhd)$_3$.

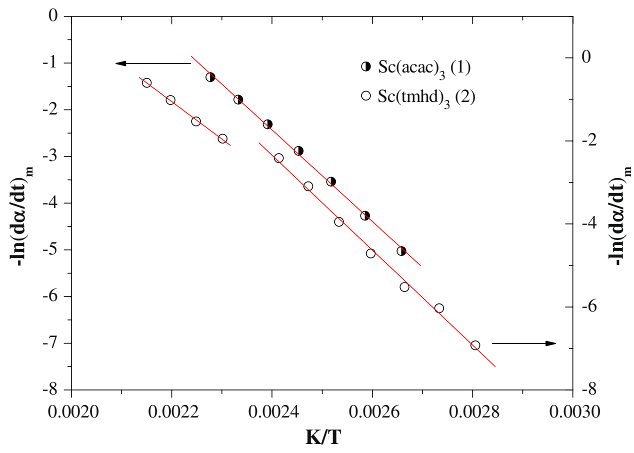

Fig. 6 Isothermal temperature based plots of ln (dα/dt)$_m$ versus 1/T for Sc(acac)$_3$ and Sc(tmhd)$_3$

Isothermal kinetics

According to the Eq. 5 the activation energy of sublimation for (1) and (2) is determined and summarized in Table 1. The activation energy for both compounds is derived from the plot of ln(dα/dt)$_m$ versus 1/T (Fig. 6). The plot of ln(dα/dt)$_m$ versus 1/T is fit for (2) with two temperature spans, which is separated by melting temperature and is represented with sublimation and vaporization kinetics of the compound. Multiplying the slope of the isothermal plots by universal gas constant (8.314 J K^{-1} mol^{-1}), values of 81 ± 2 kJ mol^{-1} (375–450 K) and 95 ± 3 kJ mol^{-1} (356–414 K) could be derived for the activation energy of isothermal sublimation for (1) and (2), respectively. The activation energy of isothermal vaporization was found to be 75 ± 3 kJ mol^{-1} (434–465 K) for 2.

Table 1 show that the two kind of non-isothermal techniques, Flynn–Wall and Kissinger, afford similar activation energies of sublimation for both scandium complexes. However, it is interesting that the activation energy values of of isothermal vaporisation (75 ± 3 kJ mol^{-1} (434–465 K)) and non-isothermal process, Flynn–Wall (73 ± 2 kJ mol^{-1}) and Friedman (79 kJ mol^{-1}) techniques afforded, almost the same as the activation energy derived by Kissinger (67 ± 5 kJ mol^{-1}) technique for precursor (2). Nevertheless, the E_a values derived for precursor (1) shows dissimilarity with the values from non-isothermal and isothermal techniques. The E_a values of precursors (1) and (2) calculated by Flynn–Wall technique, the constant E_a values over the different conversions (0.1–0.8), revealed that the non-isothermal TG processes are diffusion controlled. The above results imply that the sublimation characteristics could vary with the heating method, sample size and temperature range.

Conclusion

The sublimation and evaporation of precursors (1) and (2) were studied applying the isothermal and non-isothermal thermogravimetry measurements. The isothermal sublimation and vaporization activation energy values are found to be 81 ± 2, 95 ± 3 kJ mol^{-1}($E_{a(\text{sub})}$) for (1) and (2), 75 ± 3 kJ mol^{-1} ($E_{a(\text{vap})}$) for (2), respectively.

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