

Synthesis and thermal analysis of yttrium metallorganic complexes for evaluation as chemical vapor deposition precursors

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ABSTRACT

The thermal stability and suitability of synthesized yttrium metallorganic complexes were studied for chemical vapor deposition use by thermogravimetric analyses. The phase purity of the synthesized complexes was analyzed by powder X-ray diffraction and mass spectral techniques. The equilibrium vapor pressure of screened yttrium complexes was measured over a temperature range 319–475 K using the horizontal thermogravimetric analyzer as a transpiration apparatus. Model and model-free solid-state kinetic methods were applied to non-isothermal and isothermal measurements to derive kinetic characteristics of the sublimation/evaporation process of selected yttrium vapor sources in the conversion range of $0.1 \leq \alpha \leq 0.7$. The relevant results are discussed in detail. Copyright © 2012 VBRI Press.

Keywords: Yttrium β -diketonates; thermogravimetric analysis; enthalpy of evaporation; CVD precursors.



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of carbon and carbide thin films and their relevant applications.

Introduction

Yttria (Y_2O_3) thin film is attractive for potential applications in the areas of lasers, optics, and display devices like colour television tubes [1]. Recently, yttria thin film has become a topic of research in the broad field of sensors, catalysts, and luminescent devices. Their high thermodynamic stability makes them useful as thermal barrier or reaction barrier coatings[2]. Y_2O_3 thin films meet the above requirements because of the high dielectric constant and good crystallographic stability of up to 2598 K. Thin films of yttria have been deposited using various methods. Among them, metallorganic chemical vapor deposition (CVD) is a more attractive technique for large area growth, good film uniformity, and excellent conformal step coverage. Metallorganic precursors for CVD must display a number of important physical and chemical properties, which include sufficient volatility, solubility for liquid injection based processes, availability in significant quantities with the required low toxicity, and ligand stability such that clean metal-ligand dissociation is possible at the substrate temperature [3-6]. Essentially, the film growth rate is limited by the precursor vapor pressure. There are several methods to measure a low vapor pressure, such as the gas saturation (transpiration) method, Knudsen effusion method, and vapor pressure balance method. The conventional transpiration method is still the method of choice for determining low vapor pressures [7, 8].

Herein, we report the preparation, screening, and selection of yttrium complexes for CVD process. Prior to the vapor phase process, the vapor pressure measurements were carried out for the selected yttrium complexes using the isothermal TG-based transpiration technique in high pure nitrogen atmosphere. The non-isothermal and isothermal evaporation kinetics of tris(2,2,6,6-tetramethyl-3,5-heptanedionato)yttrium(III) were determined from the mass loss data by applying model-fitting and model-free approaches. Applicability of some of the yttrium precursors was demonstrated recently by CVD technique [9].

Experimental

Synthesis and investigation

Several yttrium complexes with acetylacetone [10], tetramethylheptanedione [11], hexafluoroacetylacetone [12], tetramethylethylenediamine [13], polyether, and amine as ligands were synthesized by adjusting the pH after mixing yttrium chloride ($YCl_3 \cdot 6H_2O$) with the corresponding ligand in ethanolic or aqueous solutions. The adduct complexes of $Y_2(tmhd)_6(A)$ (where A is diglyme or triglyme) were prepared by adopting the procedure of Drake *et al.* [14]. The resulting clear solution of $Y(tmhd)_3(H_2O)$ in hexane was added to glyme in a 1:1 mole ratio and the reaction mixture was stirred for 1 h. The solvent and liberated water were then removed under vacuum to yield a colorless oil, which was allowed to stand for 7 days during which a large crop of colorless crystalline blocks formed at 293 K.

The phase purity of the precursors was studied using X-ray diffraction analyses by an upgraded Philips PW-1730 X-ray diffraction system interfaced with VisXRD software for recording the XRD pattern by automation. Fast atom bombardment (FAB) mass spectra were recorded for $Y(tmhd)_3$ and $Y_2(tmhd)_6(triglyme)$ by JEOL SX 102/DA-6000 using argon/xenon as the FAB gas at an accelerating voltage of 10 kV with m-nitrobenzyl alcohol as the matrix at room temperature. Horizontal Perkin-Elmer Pyris-Diamond TG-DTA thermal analyzer was adopted for non-isothermal analysis of yttrium complexes. The TG measurement was carried out in a platinum crucible under high pure nitrogen, which was dried by passing through refrigerated molecular sieves (Linde 4A) with a flow rate of $12 \text{ dm}^3 \text{ h}^{-1}$ at a linear heating rate of 0.17 K s^{-1} in ambient pressure.

Vapor pressure measurements

A TG apparatus with the transpiration method for vapor pressure measurements of completely volatile β -diketonates is presented, and the apparatus is tested with benzoic acid [15]. Prior to the vapor pressure measurements, blank runs were taken with a flow rate of $12 \text{ dm}^3 \text{ h}^{-1}$ of dry nitrogen gas from room temperature to 1173 K at a rate of 15 K min^{-1} keeping both the sample and the reference pans empty. The system was then cooled to ambient temperature under the same conditions, which was done for heat cleaning of the furnace. Thereafter, the sample weighing in the range of 30–35 mg was spread out on a platinum crucible mounted for vapor pressure measurements and was carefully flushed with N_2 at a rate of $6 \text{ dm}^3 \text{ h}^{-1}$ at ambient

temperature. The flow of the carrier gas was monitored through an MKS flow controller and an MKS type 247-channel readout multi gas controller. The initial heating to 370, 360, and 310 K was rather rapid (10 K min^{-1}) and after allowing for temperature stabilization, subsequent changes in isothermal temperatures in the range of 381–473, 381–474, 370–431, and 319–351 K were done at a heating rate of 2 K min^{-1} , respectively, for yttrium complexes of $Y(tmhd)_3(H_2O)$, $Y(tmhd)_3$, $Y(tmhd)_3(\text{triglyme})$, and $Y(\text{hfac})_3$ (Table 1).

Results and discussion

Yttrium–tmhd complexes (Table 1) are completely volatile and highly soluble in the range of organic solvents. This pronounced solubility even in non-polar aliphatic hydrocarbon solvents is most likely to be due to the coordinative saturation of the metal center in these complexes. The phase purity of compounds $Y(\text{acac})_3(H_2O)_2$ (Fig. 1), $Y(tmhd)_3(H_2O)$, and $Y_2(tmhd)_6(\text{triglyme})$ was confirmed by powder XRD analyses [9]. The patterns were compared with standard PDF files.

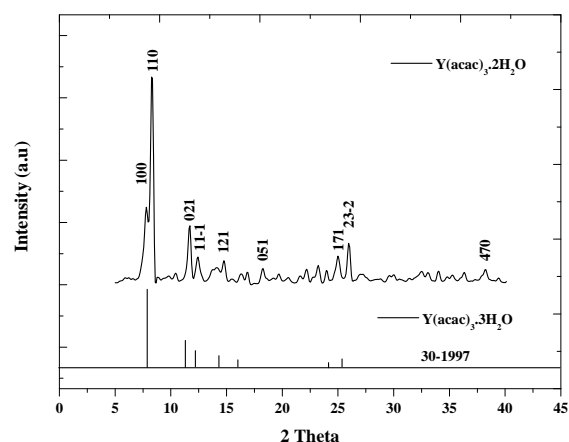


Fig. 1 Powder XRD pattern of $Y(\text{acac})_3(H_2O)_2$ (1).

The diffraction pattern of hydrated $Y(\text{acac})_3(H_2O)_2$ is shown in Fig. 1. The interplanar distance (d -space) of 10.64 \AA was observed at 2θ of 8.31° . The dehydration of $Y(\text{acac})_3$ was also assessed by IR spectroscopy and TG. The calculated unit cell parameters are $a = 11.40(2)$; $b = 29.53(5)$; $c = 8.87(2)$; $\alpha = \gamma = 90^\circ$; $\beta = 96(2)$, molecular weight = 422; space group = $P21/c$; calculated lines = 2715, number of reflections = 274. The observed full-width half-maximum (FWHM) was 0.236° at 8.31° . The average crystallite size was evaluated using Scherrer equation and found to be 33.8 nm. The volume of the unit cell and X-ray density of $Y(\text{acac})_3(H_2O)_2$ was found to be 2968.75 \AA^3 and 0.940 g cm^{-3} , respectively. Cunningham *et al.* [16], Davis and Fackler [17] described the coordination behavior of water molecules with the yttrium center. Three bidentate acetylacetonate groups and two water molecules bonded each yttrium atom to eight oxygen atoms. The third water associated with each molecule takes part in the chain of hydrogen bonds to link the molecules in pairs. The coordination polyhedron of the yttrium ion was a distorted square antiprism [16].

The measured powder XRD analysis of $Y(\text{tmhd})_3(\text{H}_2\text{O})$ and d -spacing values were quite similar with JCPDS No. 46-1989 [9]. The powder pattern of $Y_2(\text{tmhd})_6(\text{triglyme})$ was (021), (034), and (002) at 2θ values of 8.669, 9.773, and 21.712° , respectively [9]. The unit cell parameters for $Y_2(\text{tmhd})_6(\text{triglyme})$ were $a = 20.014$ (20.018 Å), $b = 20.078$ (20.078 Å), $c = 20.670$ (20.668 Å); volume of the unit cell was 8276.32 (8276.55) refined with the use of crystallographic parameters by CELREF Version 3. The estimated best space group ($P2_1/C$, indexed 111, calculated 1425) corresponds to the group having the maximum checked reflections and minimum calculated reflections. This high coordination number is common for lanthanides and other yttrium alkoxides or β -diketonates. One of the most interesting features of this structure was the triglyme acting both as a chelate and as a bridging ligand via the central ethylene bridge. The patterns revealed that the synthesized compounds have purity higher than 99%, confirmed by mass spectral and DTA analyses. The measured melting point for each prepared complex is summarized in Table 1.

Table 1. Thermal behaviour of prepared yttrium complexes.

Compound	H ₂ O loss M.Pt. Dec./Eva.			Sub/Vap	Final mass loss		Nature	End Phase
	(T/K)	(T/K)	(T/K)		(T/K)	(W%)		
1. $Y(\text{acac})_3(\text{H}_2\text{O})_2$	363	402	408, 474	-	563	29	Non-Volatile	$Y_2\text{O}_3 + \text{C}$
2. $Y(\text{acac})_3$	-	403	395, 471	-	632	45	Non-Volatile	$Y_2\text{O}_3 + \text{C}$
3. $Y(\text{acac})_2(\text{salen})$	-	496	505	-	579	15	Non-Volatile	$Y_2\text{O}_3 + \text{C}$
4. $Y(\text{tmhd})_3(\text{H}_2\text{O})$	375	445	428	432	525	100	Volatile	-
5. $Y(\text{tmhd})_3$	-	448	418	433	535	100	Volatile	-
6. $Y_2(\text{tmhd})_6(\text{diglyme})$	-	337	347, 419, 432	-	531	100	Volatile	-
7. $Y_2(\text{tmhd})_6(\text{triglyme})$	-	354	382, 448	415*	530	100	Volatile	-
8. $Y_2(\text{tmhd})_6(\text{tmeda})$	-	410	368, 442, 585	-	600	96	Volatile	-
9. $Y(\text{hfac})_3$	-	437	391, 480	354	600	96	Volatile	-

acac – acetylacetonate, salen – bis(salicylaldehyde) ethylenediamine, tmhd – tetramethylheptanedione, diglyme – diethylene glycol dimethyl ether, triglyme – triethylene glycol dimethyl ether, tmeda – tetramethylethylenediamine, hfac – hexafluoroacetylacetonate, Dec – decomposition, Eva – evaporation, Sub – sublimation, *Vap – Vaporization

The functional groups in the prepared yttrium compounds were subjected to FT-IR and NMR spectroscopy. The NMR results for complexes $Y(\text{acac})_3(\text{H}_2\text{O})_2$ and $Y(\text{tmhd})_3(\text{H}_2\text{O})$ are given below: $Y(\text{acac})_3(\text{H}_2\text{O})_2$: ^1H NMR (δ in ppm): 1.584–2.243 ($=\text{C}-\text{C}-\text{CH}_3$), 3.238–3.600 ($-\text{C}=\text{C}-\text{CH}_3$), 5.230–5.481 ($=\text{CH}-\text{C}$), 6.753 ($-\text{CH}$); ^{13}C NMR (δ in ppm): 24.83–27.46 ($-\text{C}=\text{C}-\text{CH}_3$), 30.82 ($=\text{C}-\text{C}-\text{CH}_3$), 100.45–103.54, ($-\text{C}=\text{C}-\text{CH}_3$), 190.28–191.13 ($-\text{C}=\text{O}$), and 202.04 ($=\text{C}-\text{O}$). $Y(\text{tmhd})_3(\text{H}_2\text{O})$: ^1H NMR (δ in ppm): 0.932–1.152 ($-\text{CH}_3$), and 5.452–5.730 ($-\text{CH}$); ^{13}C NMR (δ in ppm): 26.13–28.64 ($-\text{CH}_3$), 39.78–40.25 ($-\text{C}-\text{CH}_3$), 89.95–90.74, ($=\text{CH}-\text{C}$), 198.95 ($-\text{C}=\text{O}$) and 200.98 ($=\text{C}-\text{O}$).

Thermal behavior of the prepared complexes was studied by thermogravimetry over 323–632 K under dry nitrogen atmosphere (Fig. 2). The last six complexes (Table 1) exhibited substantial volatility below 600 K and $Y_2(\text{tmhd})_6(\text{A})$ showed lowest melting and 100% weight loss. The reason for the non-volatile nature of $Y(\text{acac})_3(\text{H}_2\text{O})_2$ is due to its unsaturation of coordination sphere upon heating the complex, leading to oligomerization or poor stability on heating. Enhancement

of volatility [18] requires a minimization of polarizability, dipoles, and chiefly interactions between molecules of precursors in the condensed state (e.g., H-bonding). The presence of bulky substituents on the parent β -diketonates such as Me_3C and tetramethylheptanedione sterically obstructed oligomerization and monomers are formed due to the shielding effects of these ligands [19]; bulky aromatic groups on β -diketonates prevent volatility. This is supported by the complete volatility of $Y(\text{tmhd})_3(\text{H}_2\text{O})$ in which the bulkiness is due to the methyl ($-\text{CH}_3$) groups of β -diketonate (2,2,6,6-tetramethyl-3,5-heptanedione, tmhd).

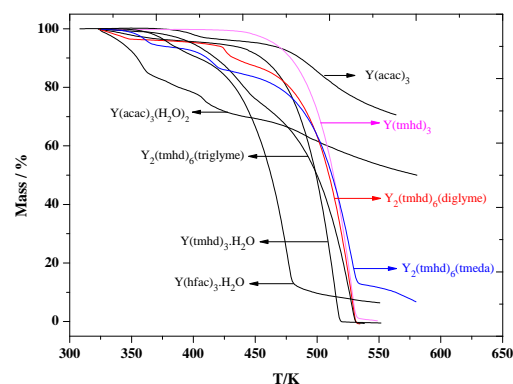


Fig. 2. TG curves of yttrium(III) complexes.

The added advantage is their excellent air/moisture stability, making it amenable for use under ambient conditions. Among the prepared complexes, $Y(\text{tmhd})_3(\text{H}_2\text{O})$, $Y(\text{tmhd})_3$, and $Y_2(\text{tmhd})_6(\text{triglyme})$ were chosen for the vapor pressure measurements, as they showed complete evaporation in TG. Owing to the volatilities of the complexes, TG-DTA results were used for the choice of the temperature range over which the vapor pressure could be experimentally determined in the present investigation. $Y(\text{hfac})_3$ was also found to be completely volatile, since the presence of fluorine in the complex is not considered for vapor pressure measurements and further CVD processes. As one of the objectives of this investigation was to evaluate the vapor pressure of the compounds by the transpiration technique, a priori knowledge of the molecular weight of the vaporizing species is required. For this purpose, compounds $Y(\text{tmhd})_3(\text{H}_2\text{O})$ and $Y_2(\text{tmhd})_6(\text{triglyme})$ were subjected to FABMS studies. The FAB mass spectrum peak at $m/z = 638$ is attributed to the molecular mass of $Y(\text{tmhd})_3$. The following peaks at $m/z = 580, 455, 397,$ and 273 were due to the fragments of $[\text{YL}_3-\text{C}(\text{CH}_3)_3]^+$, $(\text{YL}_2)^+$, $[\text{YL}_2-\text{C}(\text{CH}_3)_3]^+$, and $[\text{YL}]^+$, respectively, from the molecular ion, which confirmed the monomeric nature of $Y(\text{tmhd})_3$. The dimeric nature of $Y_2(\text{tmhd})_6(\text{triglyme})$ was established from the highest molecular mass ions observed at $m/z = 1148$ for the species of $[\text{Y}_2\text{L}_4(\text{Me}_2\text{CHOH})(\text{triglyme})]^+$, and fragment ions observed at 910, 682, 580, 455, 397, and 273 were due to the fragmentation of $[\text{Y}_2\text{L}_4]^+$, $[\text{YL}_3(\text{Me}_2\text{CH}_2)]^+$, $[\text{YL}_3-\text{C}(\text{CH}_3)_3]^+$, $[\text{YL}_2]^+$, $[\text{YL}_2-\text{C}(\text{CH}_3)_3]^+$, and $[\text{YL}]^+$. The m/z ratios are related to the isotope of greatest natural abundance ^{89}Y . The fragmentation of the complex in vacuum is still an important observation since the material

may be used under atmospheric or plasma conditions very effectively at low vacuum (10^{-3} Torr) conditions as a molecular precursor for Y_2O_3 , or other electrolytic materials such as YSZ. In addition, the passage of a stream of carrier gas through a source material in a “bubbler” or precursor pot prior to transporting the vapor phase reagent to the MOCVD reactor imposes certain requirements on the source reagent. It is essential that it have a high vapor pressure, readiness to shed the ligand in the CVD chamber, good gas phase transportability for maintaining adequate feedstock of the precursor, and an indefinite thermal stability under operating conditions. Hence, the thermal stability, vapor pressure, thermodynamic parameters, and kinetic analyses of the selected CVD precursors were evaluated by employing TG-based non-isothermal and isothermal transpiration techniques.

Vapor pressure measurements

The standard molar sublimation enthalpy 91 ± 2 kJ mol $^{-1}$ of benzoic acid determined by Selvakumar *et al* [15] using the present apparatus in the experimental temperature range agreed with the values recommended by various investigators using various techniques [20–22]. The mean value of molar sublimation enthalpy of benzoic acid from the literature data is 90 ± 1 kJ mol $^{-1}$. The testing results of the compound give us confidence in the present apparatus, which has the advantages of accurate mass loss determination, different temperature measurements within an experiment, and smaller sample amount and shorter experimental time than other such studies [15, 23].

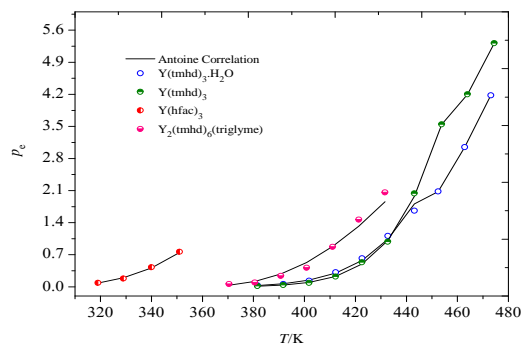


Fig. 3. Antoine correlated T–P plots for $Y(tmhd)_3(H_2O)$ (4), $Y(tmhd)_3$ (5), $Y(tmhd)_3(triglyme)$ (7), and $Y(hfac)_3$ (9).

The vapor pressure measurements are carried out at a carrier gas flow rate of 6 dm 3 h $^{-1}$. The vapor pressure so measured satisfies the conditions of equilibrium vaporization and is denoted by p_e . If W is the weight loss of the sample at the isothermal temperature caused by the flow of V_c dm 3 of the carrier gas (measured at $T_c = 298$ K), the vapor pressure p_e could be calculated using Dalton's law expression:

$$p_e = WRT_c / MV_c \quad (1)$$

where M is the molar mass of yttrium complexes $Y(tmhd)_3(H_2O)$, $Y(tmhd)_3$ or $Y_2(tmhd)_6(triglyme)$ and T_c and V_c are the temperature and volume of the carrier gas. The vapor pressure (p_e) at each saturation temperature was

calculated from the mass of the sample collected within a definite period according to the above relation. The vapor pressure as a function of temperature (**Fig. 3**) was fitted to an Antoine expression (eq 2).

$$\ln(p_e) = A - B / \left(\frac{T}{K} + C \right) \quad (2)$$

Table 2. Temperature dependence equilibrium vapor pressure (p_e)_T of $Y(tmhd)_3(H_2O)$ (4), $Y(tmhd)_3$ (5) and $Y(tmhd)_3(triglyme)$ (7).

Runs	Compound	T / K	W / mg	[(p_e)/Pa] _T
1	(4) Solid Sublimation	381.57	0.05	0.03
2		391.68	0.09	0.06
3		401.82	0.21	0.13
4		412.23	0.49	0.32
5		422.59	0.96	0.62
6		432.73	1.72	1.11
7		443.11	2.56	1.66
1	(5) Solid Sublimation	381.57	0.02	0.02
2		391.68	0.06	0.04
3		401.82	0.13	0.08
4		412.23	0.35	0.22
5		422.59	0.82	0.53
6		432.73	1.52	0.98
7		443.11	3.15	2.04
1	(7) Liquid Evaporation	370.42	0.22	0.06
2		380.53	0.32	0.09
3		390.76	0.84	0.24
4		400.85	1.47	0.42
5		411.04	3.06	0.87
6		421.32	5.16	1.47
7		431.64	7.25	2.06

The vapor pressure (p_e) result derived from the mass loss of metallorganic precursors yielded straight lines when $\ln p_e$ was plotted against $1/T$ (**Fig. 4**). The calculated linear correlation coefficients are larger than 0.97. The mass losses observed for complexes $Y(tmhd)_3(H_2O)$, $Y(tmhd)_3$, and $Y_2(tmhd)_6(triglyme)$ were in the isothermal temperature range of 319–474 K (**Table 2**). It is to be noted from the TG plots of compounds $Y(tmhd)_3(H_2O)$, $Y(tmhd)_3$, and $Y_2(tmhd)_6(triglyme)$ (**Fig. 2**) that weight loss in the complexes begins at a temperature significantly lower than the melting point and ends at a temperature higher than the melting point. Thus, below the melting point, the vapor pressure of the complexes is due to sublimation. Multiplying the slopes of Clausius–Clapeyron linear fit expressions by $-R$ (8.314 J mol $^{-1}$ K $^{-1}$), values of 97 ± 2 and 112 ± 2 kJ mol $^{-1}$ are derived for the standard molar enthalpies of sublimation ($\Delta_{sub}H^\circ$) of $Y(tmhd)_3(H_2O)$ and $Y(tmhd)_3$, respectively. The $\Delta_{sub}H^\circ$ value (112 kJ mol $^{-1}$) of $Y(tmhd)_3$ is in good agreement with 117 kJ mol $^{-1}$ reported by Tobaly *et al.* [24] based on the static technique. The enthalpies of sublimation of $Y(tmhd)_3(H_2O)$ and $Y(tmhd)_3$ were compared with the other reported values 83, 151, 136 and 142 kJ mol $^{-1}$ [25–28] and there was a considerable spread among the various determinations. Beyond the melting point, the vapor pressure is due to evaporation from the molten complex (liquid). The enthalpy of vaporization value for $Y_2(tmhd)_6(triglyme)$ was found to be

$83 \pm 3 \text{ kJ mol}^{-1}$. The congruent sublimation was verified as follows.

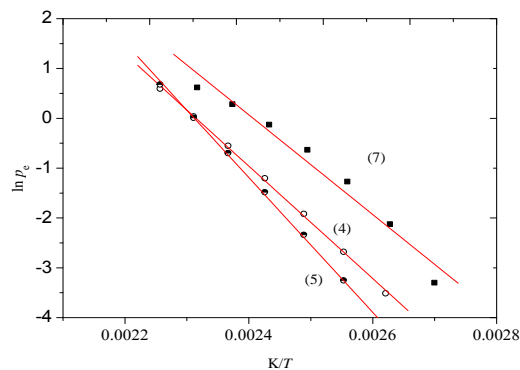


Fig. 4. Clausius–Clapeyron plots in $\ln p_e$ versus $1/T$ of $Y(\text{tmhd})_3(\text{H}_2\text{O})$ (4), $Y(\text{tmhd})_3$ (5), $Y(\text{tmhd})_3(\text{triglyme})$ (7), and $Y(\text{hfac})_3$ (9).

The FT-IR spectrum and the powder X-ray diffraction 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 sublimed product was found to have the same XRD and FT-IR as the initial product. After identifying complexes $Y(\text{tmhd})_3(\text{H}_2\text{O})$ and $Y_2(\text{tmhd})_6(\text{triglyme})$ to be ideal precursors, they were selected for the deposition of thin films by CVD [8]. The complexes $Y(\text{tmhd})_3$ and $Y_2(\text{tmhd})_6(\text{triglyme})$ are volatile, non-toxic (e.g., halogen-free), high stability toward air, light, thermal, and moisture. They exhibited a broad window of stability between the temperatures of evaporation, so that they could be efficiently transported to the deposition zone without undergoing any fragmentation en route. Because a metal-oxygen bond is already present in metal β -diketonates, the deposition of metal oxides can be theoretically achieved.

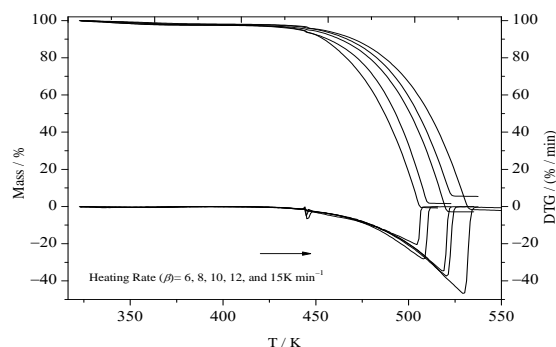


Fig. 5. Non-isothermal TG/DTG curves of $Y(\text{tmhd})_3(\text{H}_2\text{O})$ obtained at different heating rates.

Non-isothermal evaporation kinetics

It should be noted from TG (**Fig. 5**) that the experimental weight loss of 2.6% agrees with the calculated 2.7% in the temperature range of 323–355 K for the loss of one water molecule. It follows from **Fig. 4** that under non-isothermal conditions (at 6, 8, 10, 12, and 15 K min^{-1} heating rate), an intensive thermal evaporation of $Y(\text{tmhd})_3(\text{H}_2\text{O})$ starts after

melting (above 450 K), and ends completely at ~ 475 to 550 K depending upon different heating rates. The DTG curves (**Fig. 5**) show the maximal rate of increase with an increase in heating rate, indicating that the investigated process follows the single-step reaction mechanism. However, this observation is vague and further analysis is necessary.

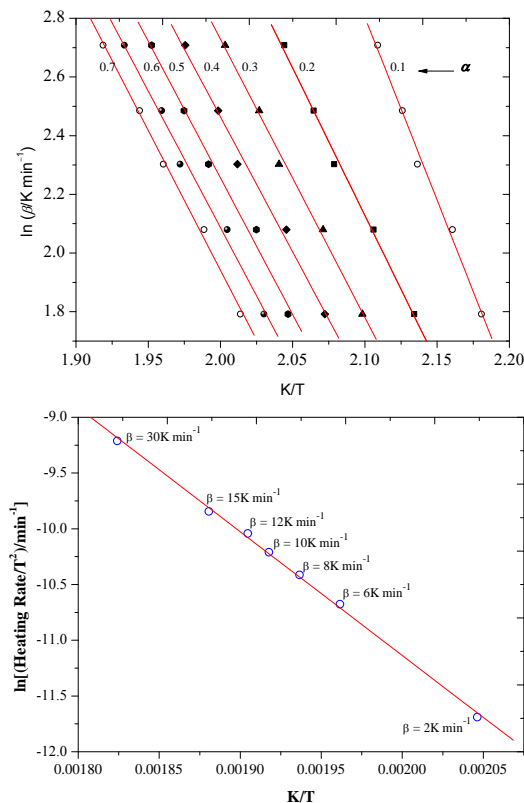


Fig. 6. Isoconversional methods for evaluating solid-state kinetics: Flynn-Wall and Kissinger plots of $Y(\text{tmhd})_3$ for a set of non-isothermal curves at 6, 8, 10, 12, and 15 K min^{-1} .

The non-isothermal conversional model fitting developed by the Coats–Redfern (CR) and isoconversional model-free methods developed by Flynn–Wall–Ozawa (FWO) and Kissinger was applied to evaluate the kinetic parameters of $Y(\text{tmhd})_3(\text{H}_2\text{O})$ evaporation. The kinetic parameters at different degrees of conversions (α) were calculated from a sample mass loss data at different heating rates ($\beta/\text{K min}^{-1}$), from the natural logarithm of heating rate temperature at which a conversion was reached at β heating rate (T), in accordance with the FWO model-free isoconversional method (eq 3).

$$\ln \beta = \text{const} - \frac{1.05 E_a}{RT} \quad (3)$$

For all sets of α values, the linear isoconversional FWO plots (**Fig. 6a**) result in linear correlation coefficients larger than 0.996. The activation energy derived from the FWO technique (93 kJ mol^{-1}) is very close to the value obtained using the Kissinger (92 kJ mol^{-1}) and Friedman

(73 kJ mol⁻¹) methods (eqs 4 and 5, respectively; **Table 3**).

$$\ln \beta = \text{const} - \frac{1.05 E_a}{RT} \quad (4)$$

$$\ln \left(\frac{\beta}{T_m^2} \right) = \ln \left(\frac{AR(n(1-\alpha))_m^{n-1}}{E_a} \right) - \frac{E_a}{RT_m} \quad (5)$$

Table 3. Activation energy (E_a /kJ mol⁻¹) of Y(tmhd)₃.

Non-isothermal				Isothermal process						
CR (R1 model)	Friedman	Kissinger	FWO	Model fitting			Isoconversional			
β	E_a	E_a	n	E_a	α	E_a	Model	E_a	α	E_a
6	79	65	0.71	79	0.1	98	F1	71	0.1	50
8	76	79	0.55		0.2	79	F2	71	0.2	55
10	73	75	0.53		0.3	75	F3	71	0.3	57
12	76	75	0.55		0.4	73	R1	71	0.4	60
15	72	72	0.54		0.5	74	R2	74	0.5	66
					0.6	74	R3	71	0.6	65
					0.7	75	A2	72	0.7	65
							A3	74		
							A4	71		
							D1	71		
							D2	71		
Average	75	73	79			78		72		60

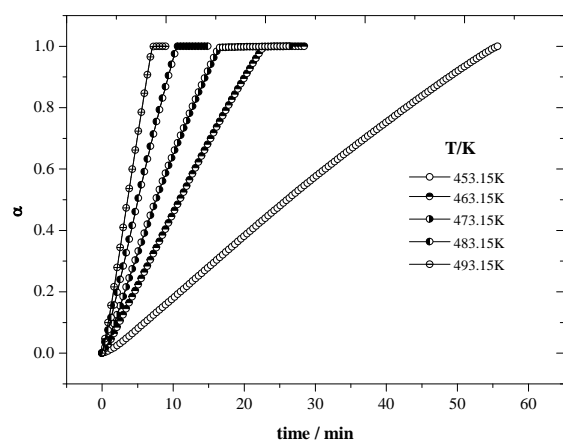


Fig. 7. Conversion (α) vs. time plots for Y(tmhd)₃

Compared to other methods, FWO and Kissinger (**Fig. 6b**) methods present the advantage that they do not require previous knowledge of the reaction mechanism for determining the activation energy [29, 30]. These results suggest that the non-isothermal sublimation process of Y(tmhd)₃(H₂O) follows a single-step gas phase reaction. The kinetic parameters for the evaporation process of Y(tmhd)₃ are determined by the CR method by using various model functions. The validity of reaction model functions was tested by a statistical *F*-test. It can be observed that only for the geometrical contraction (Rn)

models the calculated value of the apparent activation energy is nearest to the value of E_a obtained by the Flynn–Wall and Kissinger’s methods (**Table 3**). To derive the kinetic parameters of evaporation process from isothermal TG measurements, experiments were carried out at several isothermal temperatures as like section 2.2. The calculated $\alpha = f(t)$ curves are given in **Fig. 7**. The rates of conversion as a function conversion, $d\alpha/dt = f(\alpha)$, were calculated from $\alpha = f(t)$ data given in **Fig. 7**, by numerical derivation. The statistical model and model-free techniques are applied based on the $\alpha = f(t)$ curves. The Arrhenius parameters were calculated as described earlier [31, 32] and the results are summarized in **Table 3**.

Conclusion

The standard enthalpies of sublimation ($\Delta_{\text{sub}}H^\circ$) were found to be 97 ± 2 and 112 ± 2 kJ mol⁻¹ for Y(tmhd)₃(H₂O) and Y(tmhd)₃, respectively. Non-isothermal model-free techniques, such as FWO (78 kJ mol⁻¹) and Kissinger (79 kJ mol⁻¹) methods, afford similar activation energies of evaporation for Y(tmhd)₃. The kinetic data of evaporation for Y(tmhd)₃ are reported for the first time. Complete volatility and low temperature range of sublimation/vaporization below 520 K for Y(tmhd)₃(H₂O) and Y₂(tmhd)₆(triglyme) make these compounds suitable for use at a lower deposition temperature of substrate in the CVD reactor. In addition, the moderate vapor pressure and low enthalpy of Y₂(tmhd)₃(triglyme) than Y(tmhd)₃(H₂O) makes the compound more suitable for CVD from 350 K (77°C) to reap the benefits of lower deposition temperature of substrates in the CVD reactor. In addition, the better growth of Y₂O₃ is expected from Y₂(tmhd)₃(triglyme) and the same was illustrated in our earlier communication [9].

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