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Vapor pressure of tetrakis(1,1,1-trifluro-5,6-dimethylheptanedionato) zirconium(IV) and dichlorobis(η^5-cyclopentadienyl)zirconium(IV) by TG-based transpiration technique

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ABSTRACT

Zr(tfpm)$_4$ (tfpm = 1,1,1-trifluro-5,6-dimethylheptanedionate) (**1**), was prepared and characterized by FT-IR, FABMS (Mol.Wt. = 869) and TG–DTA analyses. The TG–DTA curve exhibited a single step volatilization commencing from its melting point of 121 °C and volatilizes with a nil residue at 210 °C; ZrCp$_2$Cl$_2$ (**2**) melts at 241 °C and it completely volatile at 310 °C leaving nil residue. The equilibrium vapor pressure of (**1**) and (**2**) over the range of 121.4–152 °C and 135.4–176 °C were determined to be $\log(p_e/\text{mPa}) = 12 \pm 1 - 3700 \pm 260/T$ (°C) and $\log(p_e/\text{mPa}) = 13.1 \pm 0.1 - 4533 \pm 40/T$ (°C), respectively by employing a TG-based transpiration technique. The enthalpies of vaporization ($\Delta H^\circ_{\text{vap}}$) for (**1**) and (**2**) as calculated from the slope of the curve were found to be 71 ± 5 and 87 ± 1 kJ mol^{-1}, respectively. The entropies of vaporization ($\Delta S^\circ_{\text{vap}}$) for (**1**) and (**2**) as calculated by using Trouton's rule were found to be 180.2 ± 13 and 169.3 ± 0.2 J mol^{-1} K^{-1}, respectively.

1. Introduction

Zirconia, yttria stabilized zirconia (YSZ) and scandia stabilized zirconia (ScSZ) are widely used in chemical engineering, ferroelectric dielectric films in electronics [1,2], protective coatings [3], gas sensing properties [4], catalysts [5], solid oxide fuel cells (SOFCs), oxygen sensors, memory chips, microelectronic applications due to low dielectric constant [6] and high electric conductivity. They find use in mirrors, antireflective coatings, a barrier layer between a silicon substrates and high temperature super conducting films [7]. ZrO$_2$ is an important material for the use of an alternative for SiO$_2$ as a gate dielectric in both discrete and integrated circuits [8]. The metal-organic precursors used for the CVD of ZrO$_2$ films are the amides [M(NEt$_2$)$_4$], nitrates [M(NO$_3$)$_4$], alkoxides [M(OR)$_4$], β-diketonates and mixed ligand species $[\text{M(OR)}_{4-x}(\beta\text{-dik})_x]_m$. These metal β-diketonate precursors can be sublimed at low temperature around 300 °C [9]. Among the β-diketonate complexes, the fluoro derivatives exhibit the highest volatility than the other β-diketonate derivatives [10]. The CVD of ZrO$_2$ films from volatile organic compounds using ZrCp$_2$Cl$_2$ or ZrCp$_2$(CH$_3$)$_2$ have been reported [11]. The thermochemical properties and vaporization enthalpy of the CVD precursors Zr(tfpm)$_4$ and ZrCp$_2$Cl$_2$ are hereby reported using transpiration technique using high pure nitrogen as the carrier gas.

2. Experimental

2.1. Material preparation

The chemicals 1,1,1-trifluro-5,6-dimethylheptanedione or trifluoropivaloylmethane (tfpm) (purity ≥98%, Aldrich), absolute ethanol (purity ≥99% Merck India) and zirconium tetrachloride (ZrCl$_4$) (Aldrich) and dichlorobis(η^5-cyclopentadienyl) zirconium(IV) were purchased from Aldrich (purity ≥98%). Zr(tfpm)$_4$ was prepared [12] by the reaction of ethanolic solution of ZrCl$_4$ with 1,1,1-trifluro-3,5-dimethylheptanedione under ice cold condition The compound was filtered and recrystallised from ethanol. The melting point of the complex was determined by sealing the sample in a capillary tube and is subjected to the gradual heating while in contact with the bulb of a calibrated thermometer.

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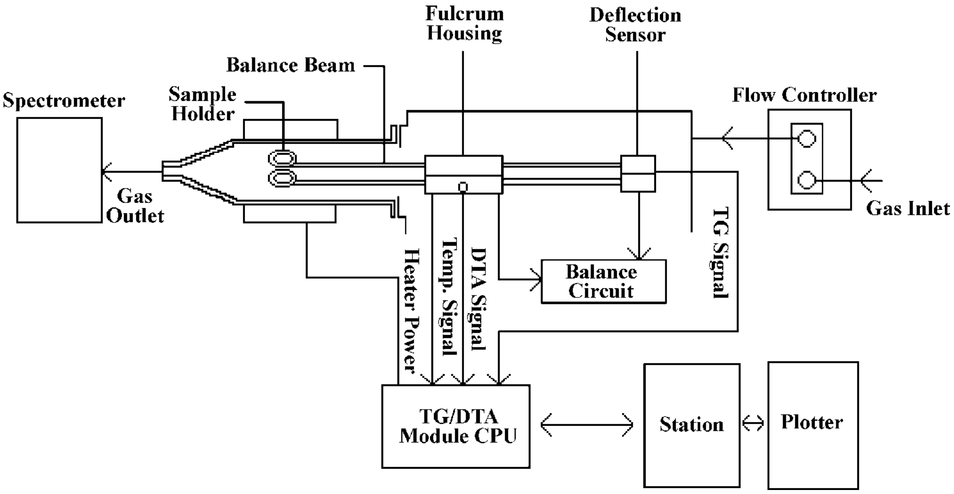

Fig. 1. Block diagram of TG-based transpiration apparatus.

The C and H analyses were carried out by CARLO-ERBA-11008 CHNS-O rapid elemental analyzer. Zirconium was analyzed by usual gravimetric method. The FT-IR spectrum was recorded using a PerkinElmer FT-IR spectrometer (RX1, FT-IR) in the region of 4000–450 cm^{-1}. The FAB mass spectrum of the complex was recorded by employing JEOL SX 102/DA-6000 spectrometer using argon as the FAB gas. An accelerating voltage of 10 kV was used with *m*-nitro benzyl alcohol (NBA) as the matrix. TG/DTA analyses of (**1**) and (**2**) were carried out in nitrogen flow of 100 ml/min at a linear heating rate of 10 °C/min from 50 to 400 °C. Thermal analyses were carried out at a linear heating rate of 0.17 °C using a TG/DTA thermoanalyzer (PerkinElmer, Pyris Diamond). High purity nitrogen (purity >99.99%) dried by passing through refrigerated molecular sieves (Linde 4 Å) was used as the carrier gas at a flow rate of 200 ml/min.

2.2. Vapor pressure measurement

The block diagram of the thermoanalyzer (Fig. 1), modification for its functioning in the transpiration mode including precise flow calibration for the carrier gas using a capillary flow meter and corrections for apparent weight loss in isothermal mode was the same as described earlier [13,14].

The configuration, calibration and cleaning of the furnace of the horizontal dual arm single furnace thermoanalyzer obviously minimizes apparent weight changes caused by temperature gradients, convection currents within the furnace tube, buoyancy, thermomolecular drag and electrostatic effect. The arms of the thermobalance served as the temperature-cum-DTA sensors. The calibration of the R type thermocouple (Pt-13% Rh/Pt) so built-in was carried out using the recommended melting point standards in order to make the T-scale to conform to the International Practical Temperature Scale 1968 (IPTS-68) amended in 1975. The finely powdered samples were spread out on a shallow alumina crucible mounted and placed on the sample pan for vapor pressure measurements. The flow rate of the carrier gas of nitrogen was varied at a rate of 100 ml/min at the ambient temperature and it was subsequently heated over the temperature range 121.4–152 °C and 135.4–176 °C in the steps approximately 10 °C. The vapor pressure measurement was carried out by using the plot of apparent vapor pressure and the flow rate. The initial heating was rather rapid (0.17 °C) and after allowing for temperature stabilization, subsequent change in isothermal steps was done at a heating rate of 0.03 °C. The choice of 100 ml/min for N_2 gas was made for the isothermal equilibrium vaporization on the basis of existence of a plateau in the plot of apparent vapor pressure (p') against the flow rate as described elsewhere [15].

3. Results and discussion

3.1. Characterization

The C and H analyses of the precursor confirmed the assigned composition of the reported literature [12]. The C, H and Zr analyses are provided. Anal.Calcd. for $ZrC_{32}H_{40}F_{12}O_8$: C, 44.08 (43.96); H, 4.62 (4.57); and Zr, 10.55 (10.46). Principal IR absorption spectral bands at 1604, 1252, 1155 and 486 cm^{-1} are assigned to γ(C—O), γ[C—$(CH_3)_3$], γ(C—F) and γ(M—O). The FABMS of (**1**) showed the peak at $m/z = 194$ due to the molecular mass of the ligand. The isotopic abundances of zirconium led to the cluster peaks at $m/z = 867$ is accounted for the molecular weight of the complex. The peaks at $m/z = 674$ and 496 are due to the fragmented species of $[ZrL_3]^+$ and $[ZrOL_2]^+$ (L = tfpm = 194).

3.2. Non-isothermal TG

The non-isothermal TG curve of $Zr(tfpm)_4$ (**1**) showed a complete weight loss (Fig. 2) in a single step commencing from 121 °C

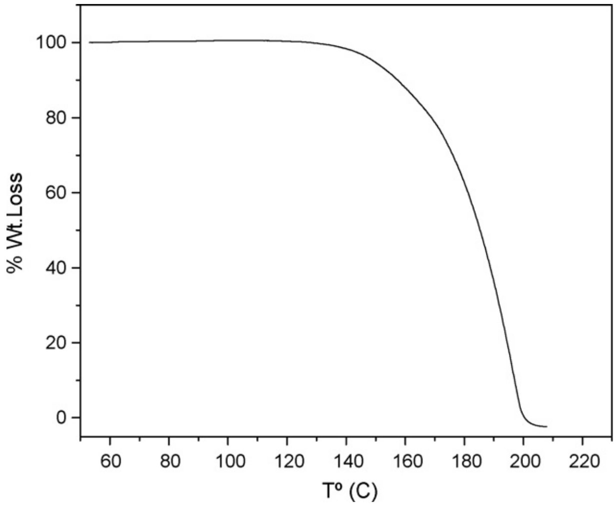

Fig. 2. TG curve of $Zr(tpm)_4$ (**1**) in N_2 atmosphere 100 ml/min at a heating rate of 0.17 °C.

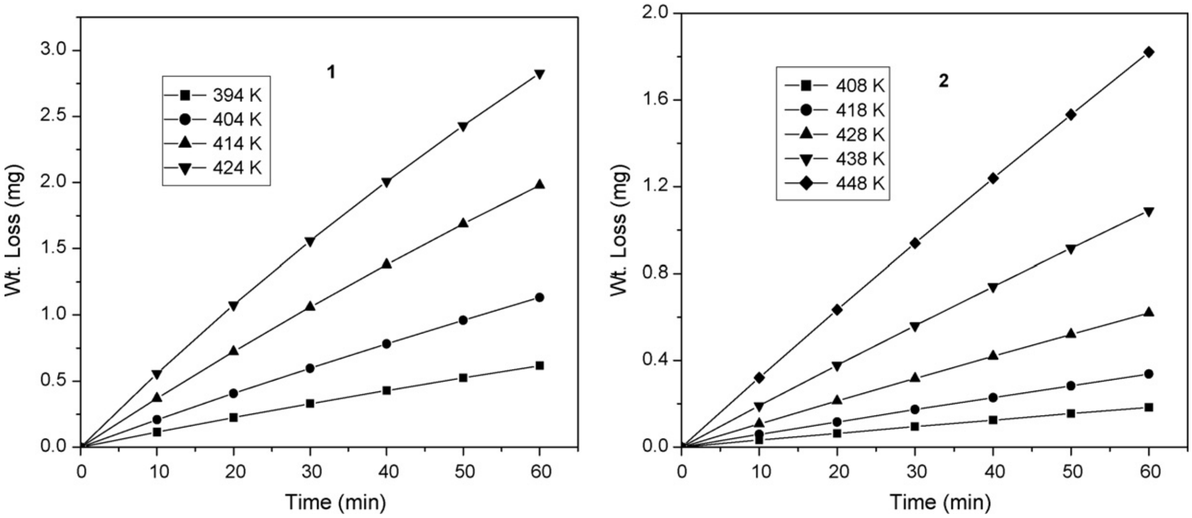

Fig. 3. Isothermal plots of time against mass loss of (**1**) and (**2**).

due to complete vaporization ending up to a total weight loss around 210 °C. The TG curve of $ZrCp_2Cl_2$ (**2**) in N_2 atmosphere revealed that the weight loss occurred in a single step as reported elsewhere [11]. The single step weight loss gives a wide temperature window for volatilization as the melting point is the important requirement for potential precursors for CVD applications.

3.3. *Vapor pressure measurement*

The rate of mass loss of a sample over a surface area under the isothermal conditions owing to the vaporization should be constant, since the vaporization is regarded as a zero order process. The TG-based transpiration technique is a convenient method to determine the vapor pressure of a congruently vaporizing species with a known molecular mass. Dalton law of partial pressure used for the calculation of vapor pressure (p_e) of the sample at the isothermal temperature is given by the relation as follows:

$$(p_e)_T = WRT_c/MV_c \tag{1}$$

M is the molecular mass of the vaporizing species, W is the weight loss of the sample at the isothermal temperature by the flow of V_c (dm^3) of the carrier gas N_2 passed at an optimum flow rate to ensure equilibrium vaporization, R is the universal gas constant as discussed elsewhere [14,15] and T_c is the temperature of the carrier gas. This equation is applicable when vapor behaves ideally, thermodynamic equilibrium is not disturbed by the flow of carrier gas and the vapor is transported by the carrier gas [16]. The isothermal TG runs for vapor pressure measurements were carried out using an optimized flow rate of 100 ml/min of N_2 to ensure equilibrium vaporization. The equilibrium conditions for vaporization of the solid samples were confirmed by the plot of isothermal weight loss (Fig. 3) against the time for each 1 h holding. The isothermal data set exhibited a linear relation R^2 and it yielded a value of 1. The observed mass loss at corresponding temperature and the calculated p_e (using Eq. (1)) are listed in Table 1.

The Clausius–Clapeyron plots of logp_e/mPa against the 1/T (K) are shown in Fig. 4. The least square analysis of log p_e against 1/T of the compounds (**1**) and (**2**) yielded the expressions (2) and (3):

$$\log(p_e/\text{mPa}) = \left(\frac{12 \pm 1 - 3700 \pm 260}{\text{T}(^\circ\text{C})}\right) \quad (121.4 - 152\,^\circ\text{C}) \tag{2}$$

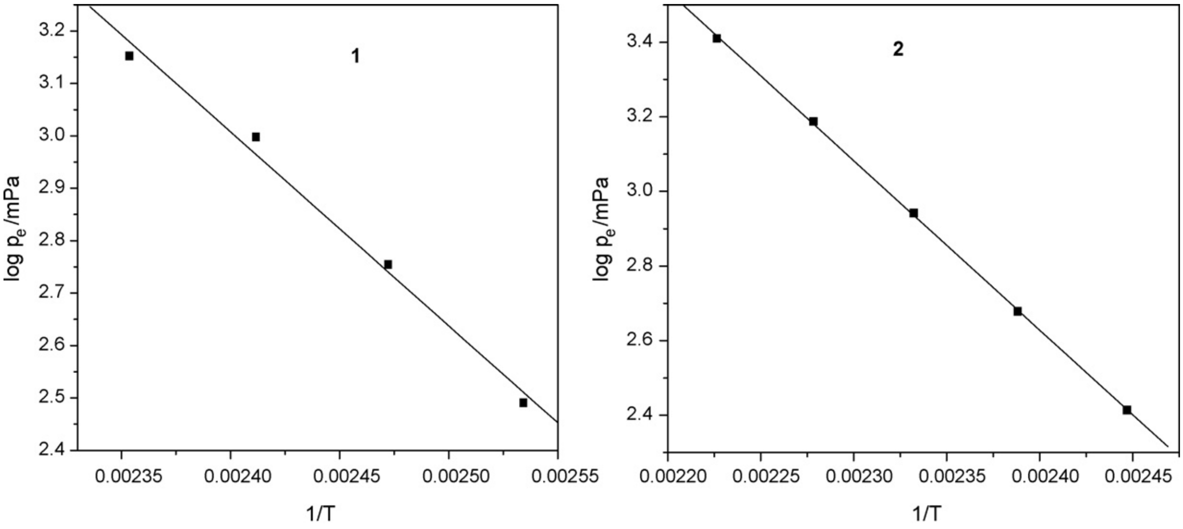

Fig. 4. Plots of log p_e against reciprocal temperature (1/T) for (**1**) and (**2**).

Table 1
Mass loss (60 min) and equilibrium vapor pressure (p_e) of (**1**) and (**2**) by the TG-based transpiration technique

S.No.	T (°C)	W (mg)	p_e/mPa
Zr(tfpm)$_4$ (**1**)			
1	121	0.6	310
2	131	1.1	569
3	142	2.0	994
4	152	2.9	1420
ZrCp$_2$Cl$_2$ (**2**)			
1	135	0.2	92
2	145	0.3	169
3	156	0.6	311
4	165	1.1	547
5	176	1.8	914

$$\log(p_e/\text{mPa}) = \left(\frac{13.1 \pm 0.1 - 4533 \pm 40}{\text{T}\,(^\circ\text{C})}\right) \quad (135.4 - 176\,^\circ\text{C}) \qquad (3)$$

Multiplying the slope of the above equation by 2.303 R, a value of 71 ± 5 and $87 \pm 1\,\text{kJ}\,\text{mol}^{-1}$ could be derived for the standard enthalpies of vaporization, ($\Delta H^\circ_{\text{vap}}$) of (**1**) and (**2**), respectively.

Thermodynamic properties of the vaporization studies of the complex (**1**) proved the assumption of the monomeric structure of the complex. The enthalpy of vaporization $71 \pm 5\,\text{kJ}\,\text{mol}^{-1}$ could be calculated for the vaporization in the temperature range of 121.4–152 °C. The vapor pressure of (**2**) was calculated in the temperature range of 135.4–176 °C and it yielded a value of $87 \pm 1\,\text{kJ}\,\text{mol}^{-1}$. The entropies of vaporization ($\Delta S^\circ_{\text{vap}}$) for (**1**) and (**2**) as calculated by using Trouton's rule were found to be 180.2 ± 13 and $169.3 \pm 0.2\,\text{J}\,\text{mol}^{-1}\,\text{K}^{-1}$, respectively.

4. Conclusion

The mass spectral analyses of (**1**) confirmed the monomeric structure and congruent nature of vaporization in the solid state. The enthalpy and entropy of vaporization values of dichlorobis(η^5-cyclopentadienyl)zirconium(IV) and tetrakis(1,1,1-trifluro-5,6-dimethylheptanedionato)zirconium(IV) have been calculated in the temperature range 135.4–176 °C and 121.4–152 °C, respectively, and the $\log p_e$ varies linearly as a function of $1/T$ by using TG-based transpiration technique. The dichlorobis(η^5-cyclopentadienyl)zirconium(IV) was identified to be completely volatile at 310 °C leaving no residue and it is a good candidate for CVD applications to make zirconia, YSZ and ScSZ films over different substrates.

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