



# Thermal analysis and vapour pressure of a new series of tungsten(VI) oxo-alkoxide- $\beta$ -ketoesterate complex precursors for the chemical vapour deposition of tungsten oxide

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## ABSTRACT

A new series of tungsten complexes, tungsten(VI) oxo-alkoxide- $\beta$ -ketoesterate complexes have been synthesized and characterized by infrared and NMR spectroscopy. Thermogravimetric analysis has been carried out on the complexes as a function of temperature, and isothermally as a function of time. Based on the thermal analysis data, these complexes are evaluated for their suitability as precursors for the chemical vapour deposition of tungsten oxide thin films. The vapour pressure of these precursors is estimated using the Langmuir equation.

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## 1. Introduction

Tungsten oxides have been studied extensively because of their possible applications in electrochromic devices [1] and gas sensors [2]. Thin films of tungsten oxide have been prepared for these applications by various physical and chemical methods of film deposition, often leading to different properties [1]. In particular, tungsten oxide thin films have been prepared by a range of chemical vapour deposition (CVD) techniques. CVD is an important method of preparation of thin films as it has advantages such as conformal coverage, high purity of films, low temperature processing and economy of large scale coatings.  $WO_3$  films have been grown by low-pressure CVD using tungsten hexacarbonyl ( $W(CO)_6$ ) as precursor [3] which is highly toxic and also using tungsten alkoxides as precursor [4]. Other precursors such as tungsten oxychloride ( $WOCl_4$ ) [5] and tungsten hexafluoride ( $WF_6$ ) [6] have also been used for CVD of tungsten oxide. However, these precursors have problems such as high reactivity, corrosivity and difficulty in handling.

In 1996, the use of volatile tungsten(VI) oxo alkoxide- $\beta$  diketone complexes of the type  $[WO(OR)_3L]$  ( $R$  = isopropyl ( $iPr$ ),

$tert$ -butyl ( $tBu$ );  $L$  = acetyl acetonate (acac), hexafluoro acetyl acetonate (hfac)) as precursors for the metal organic CVD (MOCVD) of tungsten oxide was reported [7]. However, the thermal analysis of these compounds was not reported therein, nor later in the literature. Thermal analysis of precursors is very important for their application to CVD. Furthermore, the use of fluorinated precursors for CVD has many disadvantages, due to the high toxicity and corrosivity of the fluorine. It is thus desirable to develop halogen-free precursors for CVD, and to examine their volatility through thermal analysis.

Here we report the synthesis, characterization and thermal analysis of a related series of compounds, tungsten(VI) oxo alkoxide  $\beta$ -ketoesterate complexes of the type  $[WO(OR)_3L]$  with  $R$  = isopropyl,  $tert$ -butyl;  $L$  = methyl acetoacetate (meob), ethyl acetoacetate (etob). Thermal analysis as a function of time and temperature allow us to suggest the suitability of these precursors for MOCVD applications. Further, from the differential thermogravimetry data, the vapour pressure of the precursors has been calculated with the Langmuir equation, using a recently reported procedure [8].

## 2. Experimental

The four complexes prepared and studied are  $[WO(O^tBu)_3acac]$  I,  $[WO(O^iPr)_3acac]$  II,  $[WO(O^tBu)_3meob]$  III and  $[WO(O^tBu)_3etob]$

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IV, and will be referred to henceforth by their corresponding roman numerals. The complexes were prepared by a method reported earlier for the complexes I and II ([7] and references therein), starting from tungsten oxychloride ( $\text{WOCl}_4$ ), which was prepared by reacting  $\text{WO}_3$  with  $\text{SOCl}_2$  in a sealed tube at  $200^\circ\text{C}$  [9]. The  $\text{WOCl}_4$  so obtained was dissolved in dry tetrahydrofuran (THF), and reacted with 4 equivalents of potassium *tert*-butoxide at  $0^\circ\text{C}$  to form the alkoxide complex  $[\text{WO}(\text{O}^t\text{Bu})_4]$  and precipitating  $\text{KCl}$  [10]. To this complex 1 equivalent of  $\beta$ -ketoesterate ligand was added, and the mixture warmed and stirred for 5 h. The mixture was then filtered and solvent removed under vacuum to give the final product  $[\text{WO}(\text{OR})_3\text{L}]$ .

The complexes so prepared were characterized by infrared (IR) spectroscopy on a JASCO 410 FT-IR spectrometer. NMR spectroscopy was carried out on a Bruker AMX 400 400 MHz spectrometer.  $\text{C}_6\text{D}_6$  was used as solvent and TMS was used as reference. Mass spectra of the compounds were recorded on a Micromass ESI-TOF mass spectrometer

Thermogravimetric/differential thermal analysis was carried out on the compounds, both as a function of temperature, and isothermally as a function of time at different temperatures, to examine their suitability as precursors for chemical vapour deposition. The thermal analysis was carried out on a TA Instruments SDT Q600 simultaneous DSC/TGA analyzer. All the TG experiments were carried out in flowing dry nitrogen, with a heating rate of  $10^\circ\text{C}/\text{min}$ . About 15 mg of the compound was used for the analysis, with alumina as the reference material. Isothermal experiments were carried out by ramping the temperature at  $10^\circ\text{C}/\text{min}$  to the isothermal temperature, then allowing the system to stay at that temperature for 15 min.

The Langmuir equation [8] was used to calculate the vapour pressure of the precursors.

$$P = \left[ \left( \frac{dm}{dt} \right) \sqrt{\frac{T}{M}} \right] \left[ \frac{\sqrt{2\pi R}}{\alpha_1} \right] \quad (1)$$

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

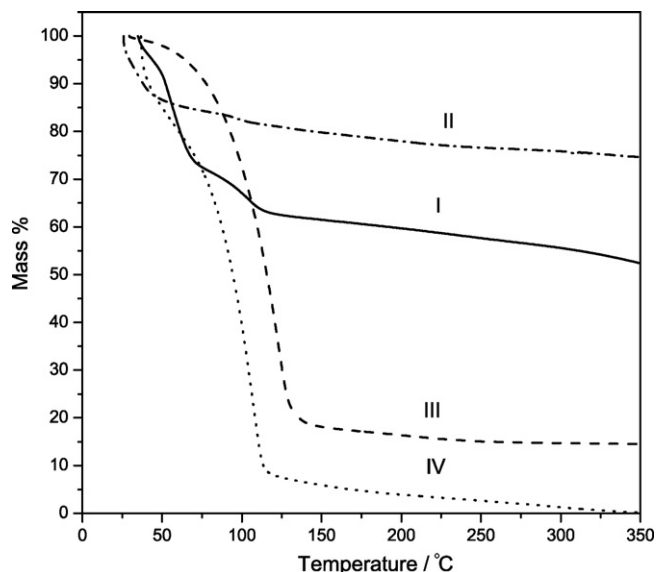


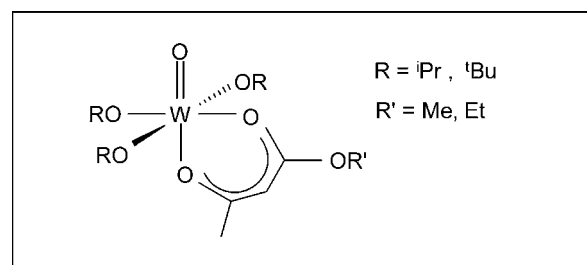
Fig. 1. TGA plot for the complexes I  $[\text{WO}(\text{O}^t\text{Bu})_3\text{acac}]$ , II  $[\text{WO}(\text{O}^i\text{Pr})_3\text{acac}]$ , III  $[\text{WO}(\text{O}^t\text{Bu})_3\text{meob}]$  and IV  $[\text{WO}(\text{O}^t\text{Bu})_3\text{etob}]$ .

$\alpha_1$  is the vapourization coefficient. In vacuum,  $\alpha_1$  is assumed equal to 1, but in the flowing gas environment of the TG experiment,  $\alpha_1$  is significantly different, and has to be determined experimentally. The term  $[\sqrt{2\pi R}/\alpha_1]$  is often referred as  $k$  in the literature. Benzoic acid was used as a standard to determine ' $k$ '. The vapour pressure for benzoic acid was taken from literature [11]. Using this value of ' $k$ ', the vapour pressure was calculated for the compounds III and IV. The Clausius–Clapeyron equation, plotted as  $\ln P$  vs.  $1/T$  gives a straight line, the slope of which is  $\Delta H/R$ , was used to obtain the enthalpy of sublimation.

The vapour pressures of complexes III and IV have been calculated using the Langmuir equation. To do so, the value of ' $k$ ' was first determined to be  $90,606 \text{ kg}^{1/2} \text{ m s}^{-1} \text{ K}^{-1/2}$ , using benzoic acid as the standard [8]. Employing this value of  $k$ , vapour pressure was calculated as a function of temperature for the complexes III and IV.

### 3. Results and discussion

The molecular structure of the complexes is shown below



The various complexes I–IV were characterized by infrared (IR) spectroscopy. The IR spectra of the complexes showed all the bands corresponding to the expected IR bands for the molecules. The IR bands for  $\text{C}=\text{O}$  and  $\text{C}=\text{C}$  of the ketoesterate ligand are observed at  $1568$  and  $1531 \text{ cm}^{-1}$  respectively. The band for the  $\text{C}-\text{O}$  and  $\text{C}-\text{H}$  are seen at  $1280$  and  $2940 \text{ cm}^{-1}$  respectively. The tungsten–oxygen bonds are observed around  $450$  and  $670 \text{ cm}^{-1}$ , confirming the formation of the complex.

The NMR spectra of the compounds I and II have been reported earlier [7]. In this work, the  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectra of the complexes III and IV were recorded using  $\text{C}_6\text{D}_6$  as solvent. The NMR data are consistent with that reported earlier for I and II [7]. The NMR data indicates the structure of the complexes to be of the type presented above. The doublet peak observed at  $\delta = 31.3 \text{ ppm}$  in the  $^{13}\text{C}$  spectrum corresponding to  $\text{CH}$  of the meob ligand indicate the structure to be as shown above. This is further supported by the presence of the singlet peak at  $\delta = 5.0 \text{ ppm}$  in the  $^1\text{H}$  NMR spectrum. All the other peaks in the  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectra can be assigned to the same structure.

The mass spectra of the compounds show all the expected fragments. Thus, the formation of these compounds is confirmed by IR, NMR and mass spectroscopy. Mass spectroscopy did not show the molecular ion peak, as the complex fragments in the high energy electron beam, but the fragments observed confirm the validity of the structure.

The weight loss of the complexes was studied as a function of temperature. The graph showing the thermograms of the complexes I–IV is given in Fig. 1. It is observed that, in the case of the  $\beta$ -diketonate complexes, the volatility is high even at relatively low temperatures. However, the volatility of the  $\beta$ -ketoesterate complexes is even higher, with weight loss of the order of 80–90% occurring in the temperature range  $50$ – $150^\circ\text{C}$ . It is also observed

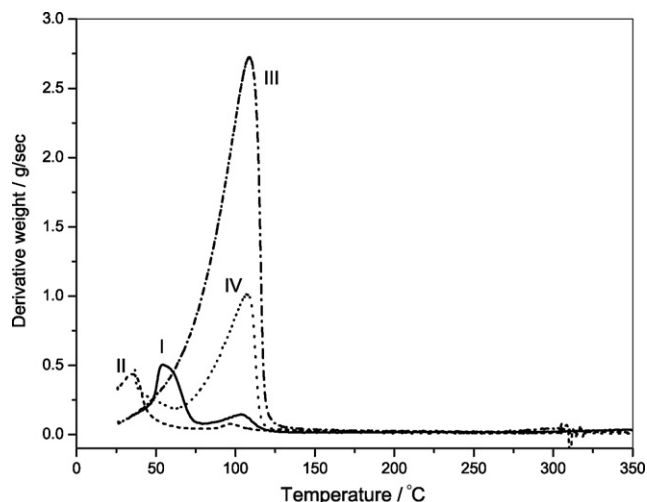


Fig. 2. DTG plots for the complexes I, II, III, and IV.

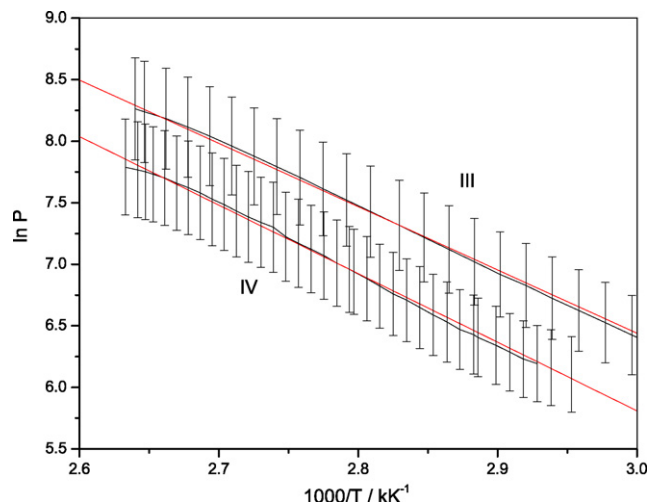


Fig. 4. Plot of  $\ln P$  vs.  $1/T$  for the complexes III and IV.

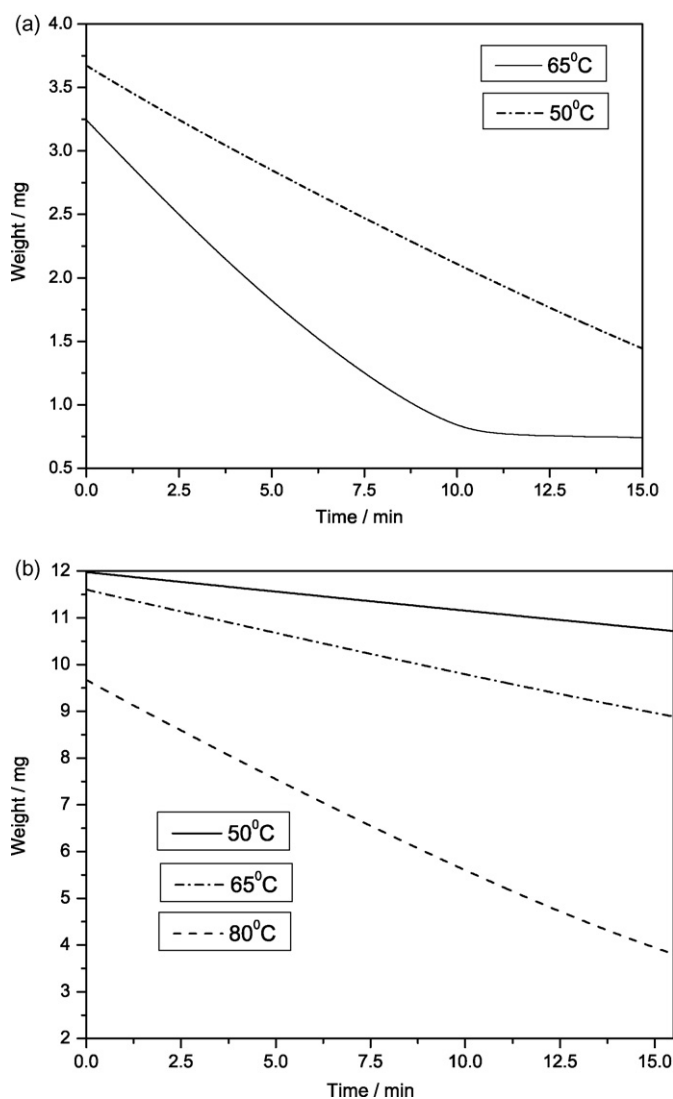


Fig. 3. (a) Isothermal TGA plots for the complex III  $[\text{WO}(\text{O}^t\text{Bu})_3\text{meob}]$ . The rate of mass loss is  $0.1247 \pm 0.0004$  mg/min at  $50^\circ\text{C}$  and  $0.2612 \pm 0.0005$  mg/min at  $65^\circ\text{C}$ . (b) Isothermal TGA plots for the complex IV  $[\text{WO}(\text{O}^t\text{Bu})_3\text{etob}]$ . The rate of mass loss is  $0.0770 \pm 0.0003$  mg/min at  $50^\circ\text{C}$ ,  $0.1640 \pm 0.0004$  at  $65^\circ\text{C}$  and  $0.3768 \pm 0.0006$  mg/min at  $80^\circ\text{C}$ .

that, as the size of the ligand L increases, the volatility of the complex increases. This is to be expected because, the larger the ligand, lower is the intermolecular interaction between adjacent molecules, and hence higher the volatility. This is seen in the thermograms of Fig. 1. The very high, single-step weight loss of the complexes III and IV indicates that they sublime, without decomposing.

The differential thermogravimetric (DTG) data are shown in Fig. 2. In case of the DTG of I and II, we see multiple peaks, indicating that many processes are involved in the weight loss step, and that the complex is probably decomposing as it evaporates. For the complexes III and IV, however, the DTG curve rises monotonically, and falls sharply to zero. This indicates that the weight loss is a single step process, and that the process is the zeroth order, i.e., the rate of weight loss is independent of the amount of material evaporating. This is a property that is highly desirable in precursors for CVD.

The weight loss of the complexes III and IV was measured isothermally at different temperatures, as a function of time. The results are shown in Fig. 3a and b. In both cases, the weight loss is linear with time. This is a very desirable property for precursors for chemical vapour deposition. The rates of weight loss are tabulated along with Fig. 3a and b respectively.

The vapour pressure data for complexes III and IV are shown in Fig. 4, as a plot of  $\ln P$  vs.  $1/T$ . The plots are straight lines, the slope of which yields the enthalpy of sublimation. From these, the enthalpies of sublimation of III and IV were calculated to be  $46.3 \pm 0.7$  and  $42.7 \pm 0.7$  kJ/mol, respectively.

The high volatility at moderate temperatures ( $50$ – $150^\circ\text{C}$ ), and the linearity of the weight loss with time, indicate that these  $\beta$ -ketoesterate complexes exhibit the characteristics required of good precursors for the chemical vapour deposition of tungsten oxide thin films. The precursors are also found to be stable for long periods, more than six months, when stored under moisture free conditions. This has been verified by carrying out thermal analysis on stored precursors, and finding that the TGA data are invariant even after six months of storage. The CVD of tungsten oxide films using these complexes as precursors is presently under way. The tungsten complexes reported here are relatively stable, and are less toxic and/or easier to handle than tungsten hexacarbonyl and tungsten alkoxide complexes that have often been used for the CVD of tungsten oxide thin films.

#### 4. Conclusion

The results indicate that of the four complexes evaluated, the two new complexes [WO(O<sup>t</sup>Bu)<sub>3</sub>meob] and [WO(O<sup>t</sup>Bu)<sub>3</sub>etob] are promising precursors for the chemical vapour deposition of tungsten oxide thin films.

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