

Thermoanalytical studies of oxovanadium(IV)hydroxamate complexes

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29th STAC-ICC Conference Special Chapter
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Abstract The thermal decomposition behavior of oxovanadium(IV)hydroxamate complexes of composition [VO(acac)(C₆H₅C(O)NHO)] (I), [VO(C₆H₅C(O)NHO)₂] (II), [VO(acac)(4-ClC₆H₄C(O)NHO)] (III), [VO(4-ClC₆H₄C(O)NHO)₂] (IV) (where acac = (CH₃COCHCOCH₃⁻) synthesized from the reactions of VO(acac)₂ with equi- and bimolar amounts of potassium benzohydroxamate and potassium 4-chlorobenzohydroxamate in THF + MeOH solvent medium has been studied by TG and DTA techniques. TG curves indicated that complexes I, II, and IV undergo decomposition in single step to yield VO₂ as the final residue, while complex III decomposes in two steps to yield VO(acac) as the likely intermediate and VO₂ as the ultimate product of decomposition. The formation of VO₂ has been authenticated by IR and XRD studies. From the initial decomposition temperatures, the order of thermal stability for the complexes has been inferred as IV > I > III > II.

Keywords Oxovanadium (IV) complexes · Potassium benzohydroxamate · 4-Chlorobenzohydroxamate · Thermal studies

Introduction

The coordination chemistry of vanadium has been the subject of continuing research interest over the years owing to the potential applications of vanadium compounds as catalysts in industry [1–4], organic synthesis [5], biological systems [6], medicine [7–9], and material science [10–16].

Literature abounds with reports on the chemistry of vanadyl ion VO²⁺, because of its affinity toward a variety of ligands to form complexes exhibiting diverse geometries around vanadium. Of numerous ligands known to form vanadium complexes, hydroxamic acids, an important family of organic bioligands, exhibiting diverse ligational behavior and possessing wide spectrum of biological activities has attracted considerable attention. Nevertheless, compared with voluminous documentation on other transition metal hydroxamates, vanadium(IV) and (V) hydroxamate complexes are rather less known [17]. Furthermore, literature contains scattered reports on the thermal behavior of complexes of vanadium despite the fact that the thermoanalytical investigations of vanadium complexes have been of considerable interest both from fundamental and technical point of view.

Like other metal complexes, it is anticipated that the final thermolysis product of vanadium complexes to be formed as oxide, may exist in either single or mixed valency states (V⁵⁺, V⁴⁺, V³⁺, and V²⁺) exhibiting structural diversity. These oxides find extensive use as catalysts, ceramic colorants, photoconductors, and gas sensors [18, 19]. In literature, the preparation of VO₂ of higher surface area (35 m²g⁻¹) has been reported from decomposition of VO-complex, (NH₄)₅[(VO)₆(CO₃)₄(OH)₉]·10H₂O at 723 K under N₂ flow at atmospheric pressure [20, 21]. Thermal treatment under vacuum at 923 K for 3 days of 1:1 mixture of V₂O₅ and V₂O₃ has also been reported to yield VO₂ [22].

Owing to the fact that VO₂ is a promising metal–insulator transition (MIT) material [23] for many electrical and optoelectrical applications such as electrical and optical switches [24, 25], tunable photonic crystals [26], and thermal imaging sensors [27], the designing of VO₂ thin films has been reported by various thin film deposition

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methods viz. e-beam evaporation [28], sputtering [29], pulsed laser deposition (PLD) [30, 31], and sol-gel [32]. The synthesis of vanadium dioxide nanowires and nanobelts has been reported from V_2O_5 xerogels and using V_2O_5 as vanadium source and $C_6H_5-(CH_2)_n-NH_2$ with $n = 2$ and 4 (2-phenylethylamine and 4-phenylbutylamine) as structure-directing templates, respectively, through hydrothermal process [33, 34]. In view of these observations and as a part of our work on the synthesis of new vanadium(IV)hydroxamate complexes [35] and to extend vanadium chemistry, we report herein, the thermoanalytical investigations of oxo-vanadium(IV) hydroxamate complexes.

Experimental

Materials and methods

Reagent grade solvents were dried and distilled prior to use. All other chemicals were reagent grade. $[VO(acac)_2]$ was prepared by reported method [36]. The potassium benzohydroxamate and 4-chlorobenzohydroxamate were synthesized by reported method [37].

TG-DTA curves of complexes were recorded on simultaneous TG-DTA SHIMADZU DT-60 thermal analyzer in air at a heating rate of $20\text{ }^\circ\text{C min}^{-1}$ using platinum crucible. Thermocouple used was Pt/Pt-Rh (10%). The temperature range of the instrument was from room temperature to $1300\text{ }^\circ\text{C}$. IR spectra of final decompositional products were recorded as KBr pellets on Nicolet-5700 FTIR spectrophotometer. The pellets were prepared in a dry box to avoid the action of moisture. X-ray diffraction pattern of thermolysed products in powdered form were recorded on Phillips PW 3071 X'PERT-PRO X-ray diffractometer (XRD) in $10\text{-}80^\circ$ 2θ range and 0.017 step sizes in continuous scanning mode at $25\text{ }^\circ\text{C}$ using Cu- $K\alpha$ radiation. Phillips X'Pert software was used to obtain precise value of parameters.

Synthesis of $[VO(acac)_{2-n}(HL^{1,2})_n]$

In a typical reaction, to a solution of $VO(acac)_2$ (1 g, 3.77 mmol) in THF (20 mL), a solution of potassium

benzohydroxamate (0.66 g, 3.77 mmol; 1.32 g, 7.5 mmol)/ potassium 4-chlorobenzohydroxamate (0.79 g, 3.77 mmol; 1.58 g, 7.5 mmol) in methanol (20 mL), was added in separate experiments. The reaction mixture was stirred for about 1 h and was then refluxed for 18–20 h. The white solid formed during the course of reaction was removed by filtration and was identified as Kacac. The filtrate was distilled off to remove excess of solvent. The concentrate was then dried under vacuum by repeatedly treating with petroleum ether, whereupon solids were obtained. These were recrystallized from dichloromethane.

Results and discussion

Complexes of composition $[VO(acac)_{2-n}(HL^{1,2})_n]$ have been synthesized according to the Scheme 1

Thermal studies

The thermal decomposition behavior of four complexes, $[VO(acac)(HL^1)]$ (I), $[VO(HL^1)_2]$ (II), $[VO(acac)(HL^2)]$ (III), and $[VO(HL^2)_2]$ (IV) has been studied by thermogravimetric and differential thermal analysis techniques in air. Thermal data of complexes is presented in Table 1. The TG curves of complexes (Figs. 1, 2, 3, 4) have shown these to be thermally stable up to 116.01 , 75.63 , 84.48 , and $137.53\text{ }^\circ\text{C}$, respectively, after which temperature the complexes (I), (II), and (IV) have been observed to decompose in single step, while complex (III) showed two step decomposition.

The mass loss of 71.01% in $116.01\text{-}521.10\text{ }^\circ\text{C}$ temperature range for complex of composition $[VO(acac)(HL^1)]$ (I) accounted for the formation of black-colored VO_2 as the final product of decomposition. The decomposition in TG was followed by endothermic peak in DTA curve at $214.33\text{ }^\circ\text{C}$.

The single step mass loss of 73.00% and 80.00%, in temperature range $75.63\text{-}511.31\text{ }^\circ\text{C}$ and $137.53\text{-}617.81\text{ }^\circ\text{C}$ in complexes of composition $[VO(HL^{1,2})_2]$, (II) and (IV), respectively, suggested the final product of decomposition as VO_2 . The complex (II) has shown a single endothermic peak at $201.97\text{ }^\circ\text{C}$. The complex (IV) has displayed two endothermic peaks at $176.29\text{ }^\circ\text{C}$, $226.91\text{ }^\circ\text{C}$ and two exothermic peaks at $421.19\text{ }^\circ\text{C}$, $493.13\text{ }^\circ\text{C}$. The schemes of decomposition of these complexes may be represented as:

Scheme 1 Synthesis of complexes

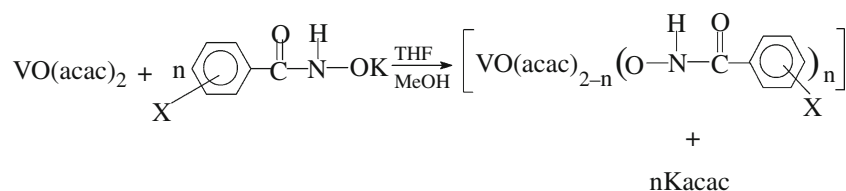
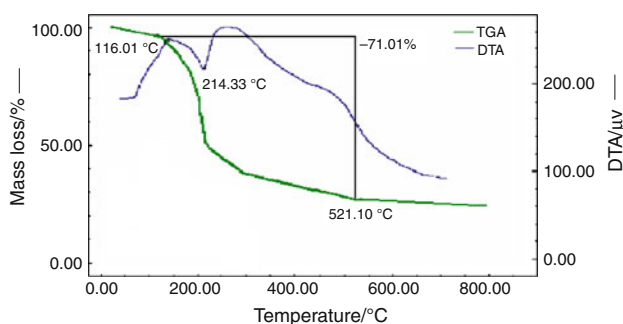
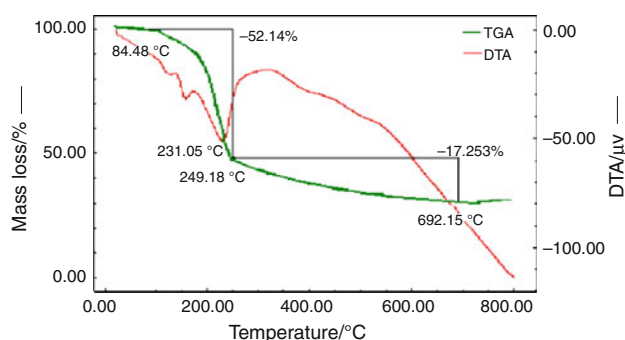
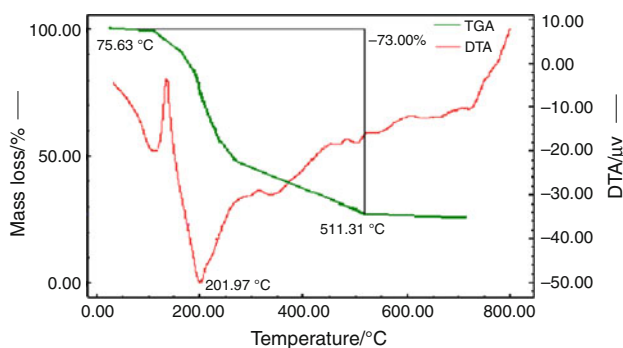
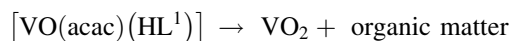
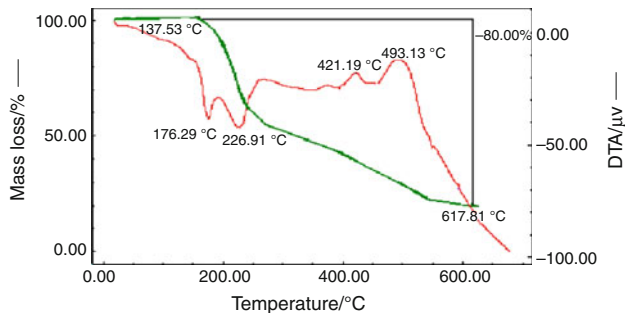


Table 1 Thermal data of oxovanadium(IV)hydroxamate complexes

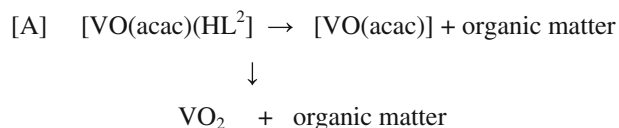
Complex	Initial decomp. Temp./°C	Stages of decomp.	TG data			DTA data	
			Decomp. Range/°C	% Mass loss Obs./Calc.	Decomp. products	Peak temp./°C	Peak nature
[VO(acac)(HL ¹)] (I)	116.01	Single	116.01–521.10	71.01 (72.52)	VO ₂	214.33	Endo
[VO(HL ¹) ₂] (II)	75.63	Single	75.63–511.31	73.00 (75.44)	VO ₂	201.97	Endo
[VO(acac)(HL ²)] (III)	84.48	1st 2nd	84.48–249.18 249.18–692.15	52.14 (50.59) 17.25 (24.70)	VO(acac) VO ₂	231.05	Endo
[VO(HL ²) ₂] (IV)	137.53	Single	137.53–617.81	80.00 (79.65)	VO ₂	176.29 226.91 421.19 493.13	Endo Endo Exo Exo

**Fig. 1** TG and DTA curves of [VO(acac)(HL¹)] (I)**Fig. 3** TG and DTA curves of [VO(acac)(HL²)] (III)**Fig. 2** TG and DTA curves of [VO(HL¹)₂] (II)

In case of complex of composition [VO(acac)(HL²)] (III), mass loss of 52.14% in temperature range 84.48–249.18 °C, in first step corresponded to the formation of VO(acac) as the probable intermediate. The mass loss of 17.23% in second

**Fig. 4** TG and DTA curves of [VO(HL²)₂] (IV)

step suggested the formation of VO₂ as the ultimate decompositional product. The DTA curve of complex (III) showed a single endothermic peak at 231.05 °C. The scheme of decomposition may be represented as:



The newly synthesized oxovanadium(IV) complexes displayed single or two stage decomposition pattern yielding VO_2 as the final product of decomposition which is quite striking as most of the vanadium complexes decompose to give V_2O_5 as the final residue. It is pertinent to mention here that the formation of V_2O_3 and VO_2 as ultimate decomposition products has been reported in the thermal decomposition of vanadium(IV) oxalate and vanadium(IV) formate, respectively.

The evidences for the formation of VO_2 as thermolysed product of oxovanadium(IV) hydroxamate complexes have been collected by recording IR spectra of residual materials and their XRD patterns.

IR Spectra

The IR spectra of powdered samples of final thermal decomposition products (Fig. 5) displayed V–O absorption bands in $1000\text{--}400\text{ cm}^{-1}$ region. The diagnostic sharp absorption band at 992 cm^{-1} attributed to $\nu(\text{V}=\text{O})$ mode is quite in agreement with the reported IR spectra of VO_2 [38]. The occurrence of absorption bands at 675 , 658 , 620 , 520 , and 322 cm^{-1} further substantiated its formation.

XRD

The thermolysed products of oxovanadium(IV) hydroxamates as powdered samples were characterized by X-ray diffraction studies and identified as VO_2 phase after having indexed all diffraction peaks (Fig. 6). A comparison of the observed hkl values with that of the reported hkl values of VO_2 films [39] has found to be in consonance with each other and consistent with a monoclinic structure (JPDs data file 44-0253).

The oxovanadium(IV) hydroxamates, thus find utility as potential precursors for the formation of VO_2 .

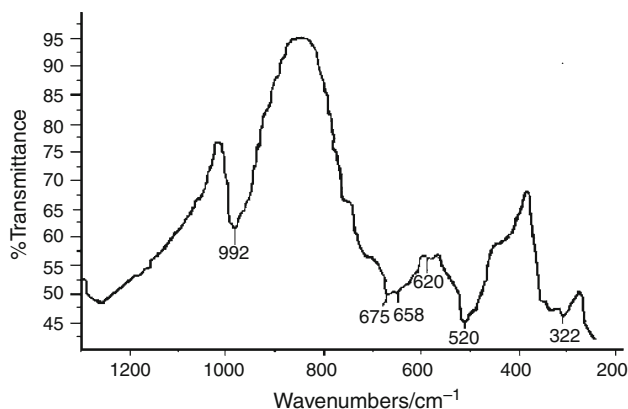


Fig. 5 IR spectrum of obtained VO_2

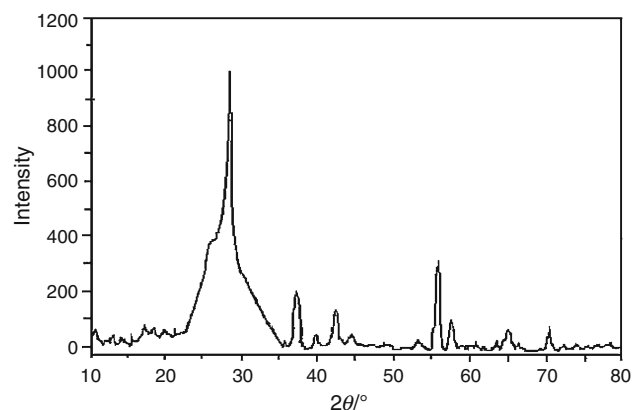


Fig. 6 XRD pattern of obtained VO_2

Conclusions

Of four oxovanadium(IV) hydroxamate complexes of composition $[\text{VO}(\text{acac})(\text{HL}^{1,2})]$ (I and II) $[\text{VO}(\text{HL}^{1,2})_2]$ (III and IV) derived from benzohydroxamate (HL^1) and 4-chlorobenzohydroxamate (HL^2) ligands, studied by TG–DTA techniques, complexes I, II, and IV have shown single stage decomposition, while complex III undergoes decomposition in two steps. On the basis of mass loss, the formation of VO_2 as the final residue has been inferred for all the complexes suggesting these as potential precursors of vanadium dioxide. The IR spectral and XRD studies of thermolysed products have authenticated the formation of VO_2 .

Acknowledgements Reena Sharma is thankful to University Grant Commission, New Delhi for providing financial support in the form of Major Research Project F. No. 33-295/2007 (SR) dated 28.02.2008. Authors thank Department of Science & Technology (DST), Government of India, New Delhi for providing financial assistance for FT-IR facility to the department. The authors also thank Sophisticated Analytical Instrument Facility, Punjab University Chandigarh, for recording XRD data

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