

Thermal studies of some biologically active oxovanadium(IV) complexes containing 8-hydroxyquinolate and hydroxamate ligands

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Abstract The thermal decomposition behaviours of oxovanadium(IV)hydroxamate complexes of composition $[\text{VO}(\text{Q})_{2-n}(\text{HL}^{1,2})_n]$: $[\text{VO}(\text{C}_9\text{H}_6\text{ON})(\text{C}_6\text{H}_4(\text{OH})(\text{CO})\text{NHO})]$ (I), $[\text{VO}(\text{C}_6\text{H}_4(\text{OH})(\text{CO})\text{NHO})_2]$ (II), $[\text{VO}(\text{C}_9\text{H}_6\text{ON})(\text{C}_6\text{H}_4(\text{OH})(5\text{-Cl})(\text{CO})\text{NHO})]$ (III), and $[\text{VO}(\text{C}_6\text{H}_4(\text{OH})(5\text{-Cl})(\text{CO})\text{NHO})_2]$ (IV) (where $\text{Q} = \text{C}_9\text{H}_6\text{NO}^-$ 8-hydroxyquinolate ion; $\text{HL}^1 = [\text{C}_6\text{H}_4(\text{OH})\text{CONHO}]^-$ salicylhydroxamate ion; $\text{HL}^2 = [\text{C}_6\text{H}_3(\text{OH})(5\text{-Cl})\text{CONHO}]^-$ 5-chlorosalicylhydroxamate ion; $n = 1$ and 2), which are synthesised by the reactions of $[\text{VO}(\text{Q})_2]$ with predetermined molar ratios of potassium salicylhydroxamate and potassium 5-chlorosalicylhydroxamate in THF + MeOH solvent medium, have been studied by TG and DTA techniques. Thermograms indicate that complexes (I) and (III) undergo single-step decomposition, while complexes (II) and (IV) decompose in two steps to yield $\text{VO}(\text{HL}^{1,2})$ as the likely intermediate and VO_2 as the ultimate product of decomposition. The formation of VO_2 has been authenticated by IR and XRD studies. From the initial decomposition temperatures, the order of thermal stabilities for the complexes has been inferred as $\text{III} > \text{I} > \text{II} > \text{IV}$.

Keywords Oxovanadium(IV) complexes · Potassium salicylhydroxamate · Potassium 5-chlorosalicylhydroxamate · Thermal studies

Introduction

Hydroxamic acids and their derivatives, the weak organic acids with low toxicity of general formula $\text{R}-\text{CO}-\text{NHOH}$

and $\text{R}-\text{CO}-\text{NR}'\text{OH}$ have extensively been studied as bioligands forming chelate complexes with numerous metals [1, 2]. The utility of hydroxamic acids as colorimetric reagents for the separation and determination of metal ions, antimalarial and tumour inhibitor drugs, enzyme inhibitors, cell division and growth factors [3–5] has also gained enormous importance. Likewise, 8-hydroxyquinoline and its derivatives constitute another group of biologically important ligands exhibiting predominantly antimicrobial activities [6–9]. These two groups of ligands have been of an enormous research interest in the coordination chemistry of vanadium owing to the role of vanadium complexes in nitrogen fixation, catalysis, design of molecular magnets, material science, as insulin mimetic, antitumour and anti-amoebic agents [10–13]. The chemistry of oxovanadium(IV) and (V) ions: VO^{2+} , VO^{3+} , VO_2^+ and $\text{VO}(\text{O}_2)^+$, in particular, because of their affinity towards a variety of ligands exhibiting diverse geometries around vanadium has attained phenomenal growth over the years. In view of the biological importance of vanadium on one hand and those of hydroxamate and 8-hydroxyquinolate ligands on the other hand and in continuation of our interest on the synthesis of new oxovanadium(IV) complexes [14, 15], we investigated the potential of unexplored $[\text{VO}(\text{Q})_2]$ as precursor towards the synthesis of mixed ligand and quinolate-free oxovanadium(IV) complexes using biologically important hydroxamate ligands viz. salicylhydroxamate and 5-chlorosalicylhydroxamate [16]. Owing to the versatility and considerable prominence of thermal methods in virtually all the branches of science and technology [17–20], it was imperative to gain an insight into the thermal behaviours of the newly synthesised complexes derived from the ligands (Fig. 1) attracted by the scattered reports in the literature on the thermal behaviours of vanadium complexes yielding V_2O_5 , V_2O_3 and VO_2 as residual

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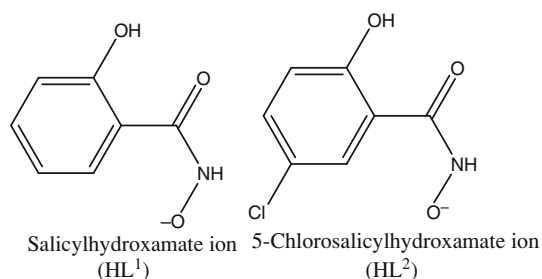


Fig. 1 Structure of ligands

products of decomposition, which find use as catalysts, gas and thermal imaging sensors, tunable photonic crystals, photoconductors and ceramic colorants [21–26].

Experimental

Materials and methods

Reagent-grade solvents were dried and distilled before use. All other chemicals were of reagent grade. $[\text{VO}(\text{Q})_2]$ as yellowish brown solid was prepared from $[\text{VO}(\text{acac})_2]$ by reported method [27]. The potassium salicylhydroxamate and 5-chlorosalicylhydroxamate were synthesised as reported earlier [28].

IR spectra of thermolysed 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. Thermograms of complexes were recorded on simultaneous TG–DTA SHIMADZU DT-60 thermal analyser in air at a heating rate of 20 °C/min using platinum crucible. Thermocouple used was Pt/Pt–Rh (10 %). The temperature range of the instrument was from room temperature to 1,300 °C. X-ray diffraction pattern of thermolysed products in powdered form were recorded on Philips PW 3071 X'PERT-PRO X-ray diffractometer (XRD) in 5–70° 2θ range and 0.017 step sizes in continuous scanning mode at 25 °C using Cu-K α radiation. Phillips X'Pert software was used to obtain precise values of parameters.

Synthesis of $[\text{VO}(\text{Q})_{2-n}(\text{HL}^{1,2})_n]$ ($n = 1$ and 2)

To a solution of $[\text{VO}(\text{Q})_2]$ (1 g, 2.81 mmol) in THF (20 mL) were added equi- and bimolar amounts of potassium

Scheme 1 Synthesis of complexes

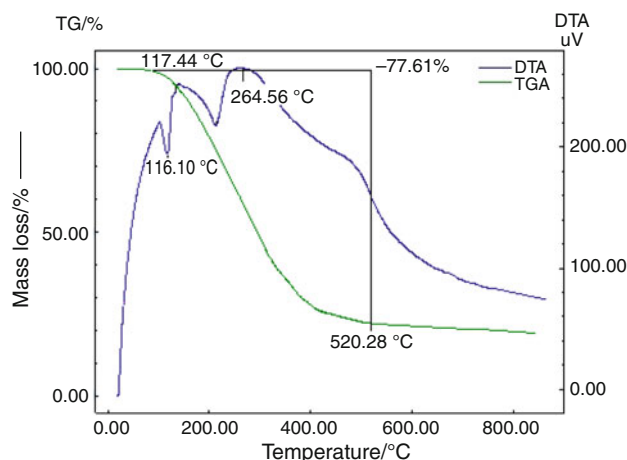
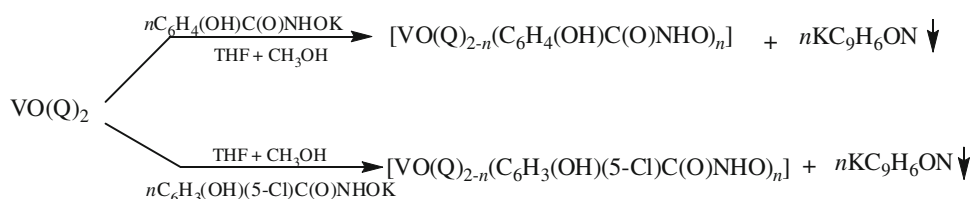


Fig. 2 TG and DTA curves of $[\text{VO}(\text{Q})(\text{HL}^1)]$ (I)

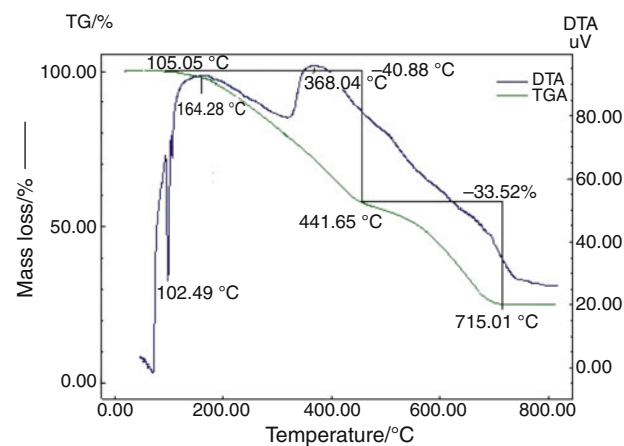


Fig. 3 TG and DTA curves of $[\text{VO}(\text{HL}^1)_2]$ (II)

salicylhydroxamate/potassium 5-chlorosalicylhydroxamate (0.54 g, 2.81 mmol/1.08 g, 5.63 mmol)/(0.63 g, 2.81 mmol/1.26 g, 5.60 mmol) in methanol (20 mL), in separate experiments. The reaction mixture was stirred for 2 h and was then refluxed for 12–16 h, during which the formation of a yellow solid anticipated as $\text{KC}_9\text{H}_6\text{ON}$ was observed. It was filtered and the filtrate was distilled off to remove excess of solvent. The concentrate was then dried under vacuum by treating it with petroleum ether whereupon black-, green- and light-brown-coloured complexes were obtained and were recrystallised from dichloromethane.

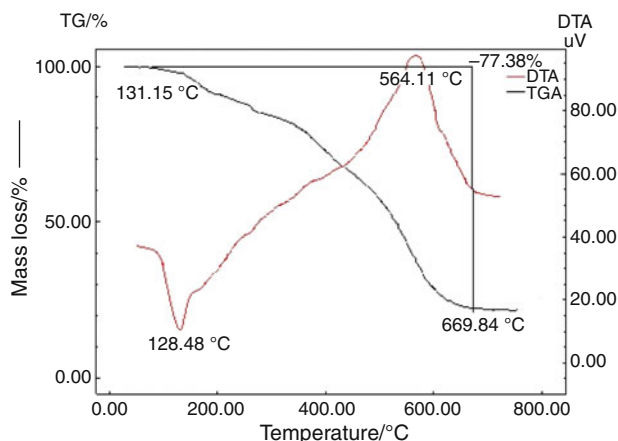


Fig. 4 TG and DTA curves of $[\text{VO}(\text{Q})(\text{HL}^2)]$ (III)

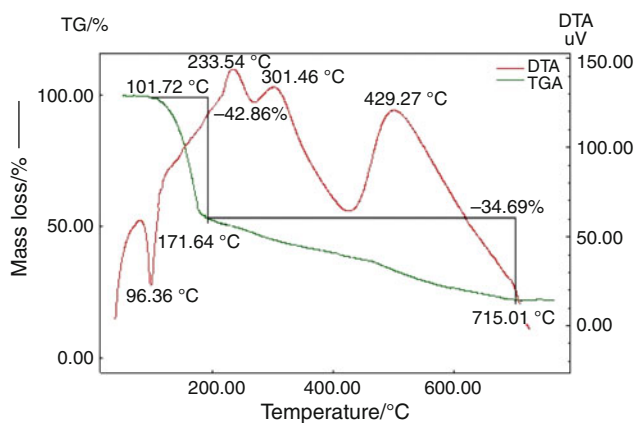


Fig. 5 TG and DTA curves of $[\text{VO}(\text{HL}^2)_2]$ (IV)

Results and discussion

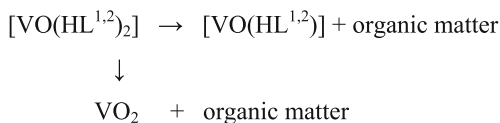
Complexes of composition $[\text{VO}(\text{Q})_{2-n}(\text{HL}^{1,2})_n]$ (I–IV) have been synthesised according to the Scheme 1.

The complexes have been characterised by elemental analyses and IR, electronic and ESR spectral studies [16].

Thermal studies

The thermal behaviour of $[\text{VO}(\text{Q})_{2-n}(\text{HL}^{1,2})_n]$ (I–IV) has been studied by TG and DTA techniques in air. The TG curves of complexes (Figs. 2, 3, 4, 5) have shown these to be thermally stable up to 117.44, 105.05, 131.15 and 101.72 °C, respectively, after which temperature complexes (I) and (III) have been observed to decompose in single step, while (II) and (IV) decompose through two step decomposition (Table 1).

The mass losses of 40.88 and 42.86 % for (II) and (IV) in first step indicated by the feeble inflexion in TG curves corresponded to the formation of $[\text{VO}(\text{HL}^1)]$ and $[\text{VO}(\text{HL}^2)]$, respectively, as the probable unstable intermediates which undergo continuous mass loss in the second step. The mass losses of 33.52 and 34.69 % in the second step for respective complexes accounted for the formation of VO_2 as the ultimate decomposition product in each case. The general scheme of decomposition may be represented as



Complexes of composition $[\text{VO}(\text{Q})(\text{HL}^1)]$ (I) and $[\text{VO}(\text{Q})(\text{HL}^2)]$ (III) have been observed to decompose in

Table 1 Thermal data of oxovanadium(IV) complexes

Complex	Initial decomposition temperature/°C	Stages of decomposition	TG data			DTA data					
			Decomposition range/°C	% Mass loss	Decomposition products	Peak temperature/°C	Peak nature				
$[\text{VO}(\text{Q})(\text{HL}^1)]$ (I)	117.44	Single	117.44–520.28	77.61	VO_2	116.10	Endo				
						264.56	Exo				
$[\text{VO}(\text{HL}^1)_2]$ (II)	105.05	First	105.63–441.65	40.88	$[\text{VO}(\text{HL}^1)]$	102.49	Endo				
		Second	441.65–715.01	33.52	VO_2	164.28	Exo				
$[\text{VO}(\text{Q})(\text{HL}^2)]$ (III)	131.15	Single	131.15–669.84	77.38	VO_2	368.04	Exo				
						564.11	Exo				
$[\text{VO}(\text{HL}^2)_2]$ (IV)	101.72	First	101.72–171.64	42.86	$[\text{VO}(\text{HL}^2)]$	96.36	Endo				
						Second	171.64–715.01	34.69	VO_2	233.54	Exo
										301.46	Exo
						429.27	Exo				

single step, and the mass losses of 77.61 and 77.38 % accounted for the formation of VO₂ as the final product of decomposition.



Compared to the formation of V₂O₅ as the final product of decomposition in most of the vanadium complexes, the formation of VO₂ in complexes under study is in agreement with our earlier observations [17, 18]. The evidences for the formation of VO₂ as thermolysed product of oxovanadium(IV) hydroxamate complexes have been gathered by means of recording IR spectra of residues. The IR spectra and XRD studies of powdered samples of final thermal decomposition products were in agreement with previous reports [29, 30]. The newly synthesised oxovanadium(IV) complexes under study thus constitute as potential precursors for the formation of VO₂.

The DTA curves of complexes (I–IV) were exhibited endothermic peaks at 116.10, 102.49, 128.49 and 96.36 °C corresponding to the melting points for the respective complexes. The complexes of composition [VO(Q)(HL^{1,2})] (I, III) showed an exothermic peak at 264.56 and 564.11 °C, respectively. Complexes [VO(HL^{1,2})₂] (II, IV) exhibited exothermic peaks at 164.28, 368.04 °C and 233.54, 301.46 and 429.27 °C.

Conclusions

The study of thermal behaviours of oxovanadium(IV) complexes of composition [VO(Q)_{2-n}(HL^{1,2})_n] (I–IV) by TG/DTA techniques showed single-step decomposition for mixed ligand complexes of composition [VO(Q)(HL^{1,2})] (I) and (III) to yield VO₂ as the final decomposition product. The quinolate-free, bis(hydroxamato) oxovanadium(IV) complexes [VO(HL^{1,2})₂] (II) and (IV) decomposed in two stages, yielding [VO(HL^{1,2})] as intermediate and VO₂ as the ultimate product of decomposition. The formation of VO₂ is indicative of the potential of parent complexes as likely precursors of VO₂.

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