



Effect of alkali metal ion and hydrogen bonds on thermal stability of $M[\text{VO}(\text{O}_2)_2\text{bpy}] \cdot n\text{H}_2\text{O}$ ($M = \text{Li}^+ - \text{Rb}^+$) and $\text{Cs}[\text{VO}(\text{O}_2)_2\text{bpy}] \cdot \text{H}_2\text{O}_2$ complexes

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ABSTRACT

The compounds $M[\text{VO}(\text{O}_2)_2\text{bpy}] \cdot n\text{H}_2\text{O}$ ($M = \text{Li}^+ - \text{Rb}^+$) and $\text{Cs}[\text{VO}(\text{O}_2)_2\text{bpy}] \cdot \text{H}_2\text{O}_2$ were characterized by thermogravimetry (TG). In the course of TG experiments, performed from 25 up to 550 °C, three main stages of decomposition were observed: (i) dehydration, (ii) releasing of the oxygen molecules and (iii) decomposition of bpy. The final product of decomposition is MVO_3 , with small amounts of paramagnetic vanadium(IV) species. Volatile products were detected on-line using mass spectrometer. Mechanism of the decomposition is discussed on the basis of crystal structures of complexes. The main role is played by hydrogen bonds involving peroxo ligands and polarising power of alkali metal ions.

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1. Introduction

Polyoxoperoxometalates are members of a large class of oxidants. Peroxo compounds of d-electron metals have attracted great attention in last years. They can take part in oxidation processes of different inorganic and organic substrates like sulphides, sulphur dioxide, alkenes, alcohols, aromatic and aliphatic hydrocarbons and phosphines [1–3]. These compounds show the ability to release active oxygen forms which also can take part in oxidative processes. These reactions, either stoichiometric or catalytic are carried out in mild conditions with good yield and selectivity.

The peroxo complexes of transition metals are thermolabile in solid phase. Usually, they vigorously decompose (sometimes explosively) with liberation of oxygen. Small gaseous molecules as e.g.: H_2O , CO_2 , CO , N_2 , NO_x , can also be released depending on organic ligand or counter-ion present [4,5]. The final products are an appropriate d-metal oxide (e.g.: Nb_2O_5) or a simple salt (e.g.: K_2WO_3 , K_2MoO_3 , $\text{Bi}_2\text{Ti}_2\text{O}_7$, $\text{K}_2\text{Ti}_2\text{O}_5$). The stability of such peroxo compounds can be enhanced by changing and/or modifying the organic ligand [6].

Peroxo complexes of vanadium received special attention because of their anti-tumor and insulin-mimetic activities and their use as functional models for the vanadium haloperoxidase enzymes [7–10].

These complexes release peroxidic oxygen in the temperature range 25–210 °C depending on the heteroligand [11–22]. For hydrated compounds this process can proceed simultaneously with water release or as a separate step following dehydration. In the latter case the lower temperature of the peroxo ligand decomposition was observed for compounds showing the lower temperature of water release [23]. Usually V_2O_5 or proper metavanadate are the final solid residue.

Although over 60 peroxo-containing vanadium(V) complexes are known [24], still there are not many comprehensive studies on thermal stability in solid phase. Moreover, the product analysis was limited to solid residue (IR and powder X-ray diffraction methods). Behaviour of vanadium peroxo complexes in solid state at elevated temperatures is important for establishing optimal storage conditions in context of their possible application as anti-tumor or insulin-mimetic drugs. The peroxo complexes of vanadium have often been used in biological and medical experiments so that their behaviour in solid state at elevated temperatures is important.

In this paper the results of thermal decomposition of bisperoxovanadates in solid state with on-line detection of gaseous products and analysis of solid residue using IR and e.s.r. methods are presented. The effect of the alkali metal ion (M) and the hydrogen bonding network on their thermal stability is discussed.

2. Experimental

The preparation details of the complexes $\text{Li}[\text{VO}(\text{O}_2)_2\text{bpy}] \cdot 5\text{H}_2\text{O} - \text{LibpV}$, $\text{Na}[\text{VO}(\text{O}_2)_2\text{bpy}] \cdot 8\text{H}_2\text{O} - \text{NabpV}$, $\text{K}[\text{VO}(\text{O}_2)_2\text{bpy}] \cdot 4\text{H}_2\text{O} - \text{KbpV}$, $\text{Rb}[\text{VO}(\text{O}_2)_2\text{bpy}] \cdot 4\text{H}_2\text{O} - \text{RbbpV}$, $\text{Cs}[\text{VO}(\text{O}_2)_2\text{bpy}] \cdot \text{H}_2\text{O}_2$ are given in the text.

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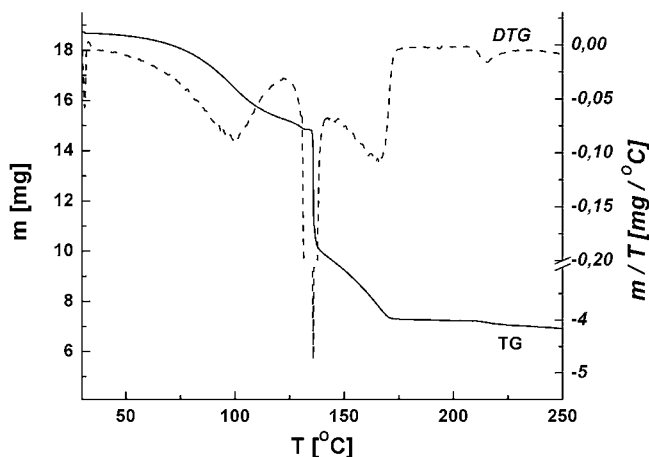


Fig. 1. TG and DTG curves for LibpV.

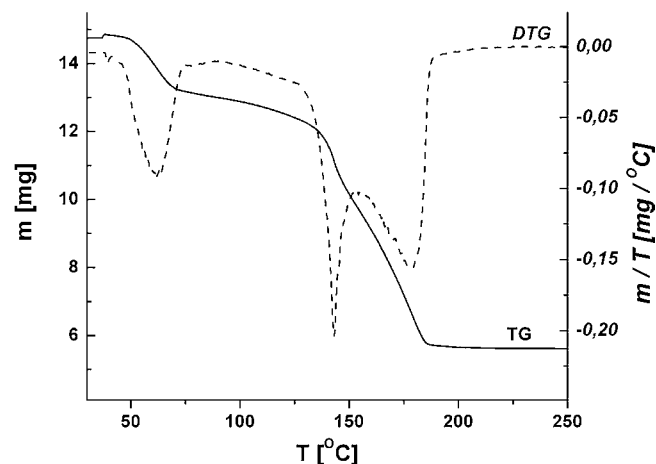


Fig. 3. TG and DTG curves for KbpV.

$\text{H}_2\text{O}_2\text{-CsbpV}$ were previously described and were characterized by single crystal X-ray structure analyses [25].

Thermogravimetric analyses were performed on a TGA/SDTA 851^e Mettler Toledo apparatus. The studied complexes were placed in open alumina crucibles (150 μl) and were heated from 25 to 550 °C with constant heating rate 10 °C/min under Ar flow (80 ml/min). The temperature was measured by a Pt-Pt/Rh thermocouple with the accuracy of ± 0.5 °C. The evolving gas was simultaneously analysed by on-line a Balzer GSD 300T quadrupole mass spectrometer (QMS) operated in electron impact (EI) mode using channeltron as a detector. Screening analyses were performed in the selected-ion monitoring (SIM) mode. The ions characteristic of each compound such as 16, 17, 18 for water, 32 for oxygen and 28 (CO), 44 (CO₂), 30 (NO) for products of decomposition of the 2,2'-bipyridine were monitored.

Infrared spectra (in nujol and KBr pellets) were collected on a Bruker IFS instrument (400–4000 cm^{-1}). The electron paramagnetic resonance spectra were taken at room temperature on an EPR ELEXSYS E-500-10/12 (Bruker) spectrometer.

3. Results and discussion

The TG and DTG curves for the hydrated complexes ($M = \text{Li}^+ - \text{Rb}^+$) are shown in Figs. 1–4. In all cases the SDTA curves are omitted for clarity. Data for the temperatures of thermal transitions and mass loss determination are given in Table 1 together with the evolved gaseous products recorded by QMS. An example of the mass spectrometry result is shown in the Fig. 2b.

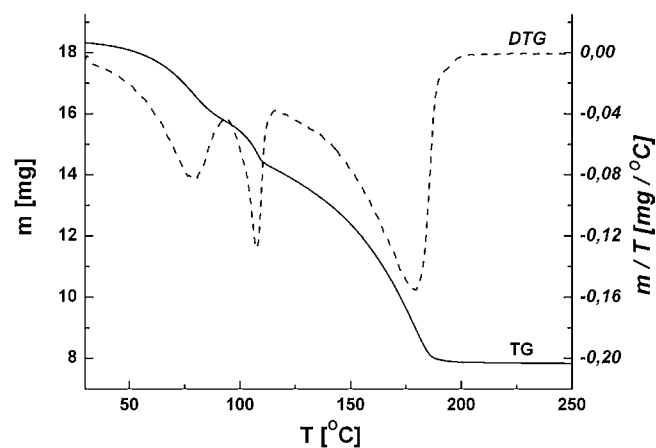


Fig. 4. TG and DTG curves for RbbpV.

All samples show three main stages of the mass loss, as indicated by peaks in the DTG curves, at temperatures dependent on the degree of hydration and the type of alkali metal ion. The individual stages are overlapping to some extent.

The first endothermic stage beginning at room temperature is associated with the loss of a part of crystallization water (all water in the case of the potassium salt). No other gaseous products were recorded by QMS spectrometry. The stoichiometry of this stage can

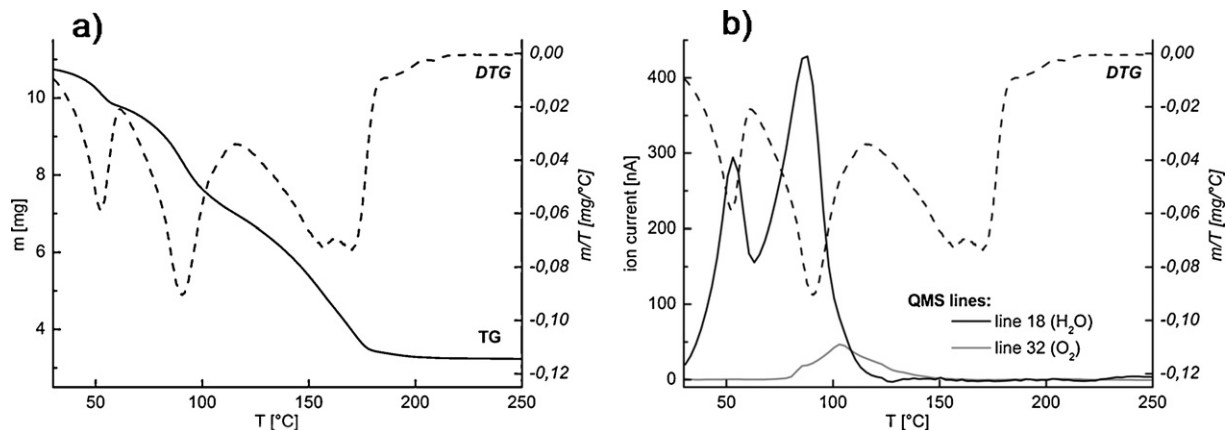


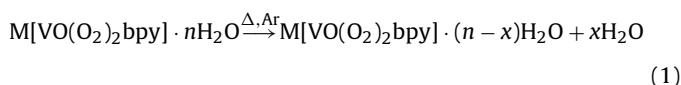
Fig. 2. TG and DTG curves for NabpV (a) and the mass spectra for selected ions (b). The QMS curves for 2,2'-bpy decomposition products are omitted for clarity.

Table 1
Thermal data for the decomposition of $M[\text{VO}(\text{O}_2)_2\text{bpy}] \cdot n\text{H}_2\text{O}$ ($M = \text{Li, Na, K, Rb}$) and $\text{Cs}[\text{VO}(\text{O}_2)_2\text{bpy}] \cdot \text{H}_2\text{O}_2$.

Complex	Temp. range (°C)	DTG peak (°C)	SDTA (stage)	Obs. wt. loss $\Delta m/m$ (%)	Calcd. wt. loss $\Delta m/m$ (%)	Evolution of (according to MS spectra)
LibpV	25–123	99	Endo (I)	18.2	18.8	4.0H ₂ O
	123–144	136	Exo (II)	29.2	29.3	H ₂ O + O ₂ + 0.4bpy (CO ₂ , CO, NO) ^a
	144–550	166	Endo (III)	25.2	24.4	0.6bpy
NabpV	25–61	52	Endo (I)	9.5	9.9	2.5H ₂ O
	61–116	91	Endo (II)	27.4	27.1	5.5H ₂ O + 0.75O ₂
	116–161	158	Endo (II)	21.2	20.7	0.25O ₂ + 0.55bpy
	161–550	170	Endo (III)	16.3	15.5	0.45bpy
KbpV	25–125	62	Endo (I)	18.3	18.1	4.0H ₂ O
	125–153	143	Exo (II)	15.6	15.9	O ₂ + 0.2bpy
	153–550	179	Endo (III)	29.8	29.8	0.76bpy
RbbpV	25–94	79	Endo (I)	14.1	14.2	3.5H ₂ O
	94–116	107	Exo (II)	8.4	9.2	0.5H ₂ O + O ₂
	116–550	179	Endo (III)	35.5	35.1	bpy
CsbpV	90–137	130	Exo (I)	10.1	10.0	H ₂ O + 0.85O ₂
	137–161	150	Exo (II)	14.8	14.9	0.65O ₂ + 0.3bpy
	161–550	186	Endo (III)	25.7	24.1	0.7bpy

^a Decomposition products of 2,2'-bpy.

be described by the following dehydration equation:



where x is the number of released water molecules.

Generally, on the basis of the DTG peak position, we can say that complexes with larger number of crystallization water molecules are less stable. The most hydrated sodium salt is the least stable complex under investigation. Lack of consistent changes in the DTG peak positions with the number of water molecules suggests that other parameters such as the type of M^+ counter cation can also affect the dehydration process. Both parameters influence the hydrogen bond network in the solid state of the complexes (see [24,25] for discussion of crystal structures of the complexes). Different DTG peak positions for isomorphous salts (with the same number of water molecules): K (62 C) and Rb (79 C) can be explained by lower strength of H-bond between the lattice water molecules of the K salt because of higher polarising effect of K on oxygen of water molecules belonging to the metal coordination sphere.

The second decomposition stage is characterized by the evolution of oxygen in one or two (in the case of Na salt) steps which is accompanied by the evolution of water and/or 2,2'-bpy. Actual products of its redox decomposition (CO₂, CO, N₂) depend on the complex. For all complexes, except for the Na salt, the exothermic process was observed as expected. The discrepancy for the Na salt stems from overlapping endothermic processes of the dehydration (5.5 mol) or liberation of 2,2'-bpy (0.55 mol) with the relatively weak exothermic process of the oxygen liberation (0.75 and 0.25 mol, respectively).

In the third stage, with temperature range up to 550 C, only 2,2'-bpy and its decomposition gaseous products (CO, CO₂ or N₂) are released.

The TG and DTG curves for the $\text{Cs}[\text{VO}(\text{O}_2)_2\text{bpy}] \cdot \text{H}_2\text{O}_2$ are shown in Fig. 5 and the data obtained from the experiments is given in Table 1.

The caesium salt solvated with the H₂O₂ instead of water molecules is the most stable among investigated complexes with the first stage DTG peak position at 130 C. In this stage the oxygen and water detected as the volatile products were formed by the exothermic disproportionation reaction of the solvated H₂O₂ according to the reaction: $\text{H}_2\text{O}_2 = \text{H}_2\text{O} + 0.5 \text{O}_2$. Some amount of peroxidic oxygen (from coordinated O₂²⁻) is also detected. The next two stages are similar to the stages of the solvated complexes.

In all cases the main final solid residue was MVO₃, confirmed by the presence of $\nu(\text{VO}_2)$ bands in their IR spectra, with small amounts

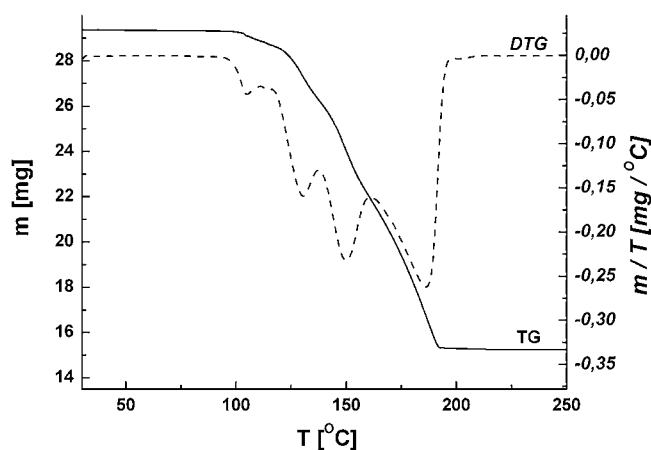
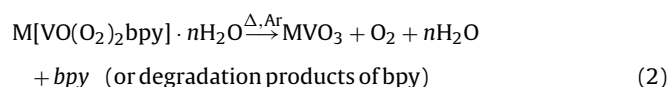


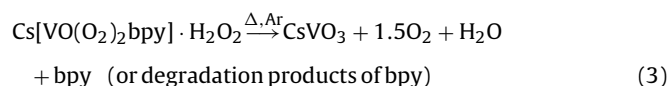
Fig. 5. TG and DTG curves for CsbpV.

of V(IV), which was confirmed by e.s.r. spectroscopy (discussed below).

Thus, the main total degradation process is postulated as:



and for cesium salt:



Analyzing the thermogravimetric data of the compounds it can be concluded that the thermal stability depends on: (i) the number of lattice water molecules, as the most hydrated sodium salt is the least stable complex under investigation (however, clear correlation between the number of water molecules and thermal stability was not found), (ii) the type of lattice solvent molecules, as the Cs salt with H₂O₂ instead of H₂O was found to be the most stable complex, and (iii) type of the counter ion (as shown by comparing the isomorphous K and Rb salts).

Generally, thermal stability of complexes depends on coordination geometry, type of coordinated ligands and on the network of hydrogen bonds [26].

All investigated complexes reported in this paper have the same ligands and the same inner coordination sphere, containing vanadium (coordination number 7) in the centre of distorted pentagonal

bipyramid, and differ only in the type of the counter ion and the type and number of lattice solvent molecules (for X-ray details see [25] and Supplementary data where the CIFs are given). Hydrogen bonds play a very important role in stabilizing crystal structures. Two types of hydrogen bonds are present in these compounds: (i) formed between water molecules and (ii) formed between a water molecule and an oxygen atom of a peroxy group.

The thermal stability of the hydrated complexes with respect to the loss of water depends on hydrogen bond network composed mostly of water molecules. During heating, the weakest hydrogen bonds are broken first, the crystal structure becomes unstable and water molecules are released in the first stage (dehydration). The observed order of the DTG peak positions for Na (52 C) < K (62 C) < Rb (79 C) < Li (99 C) salts coincides with the ordering of the D...A distances (longer distance = weaker hydrogen bond) of the weakest hydrogen bond in Na (2.823 Å) > K (2.726 Å) > Rb (2.711 Å) > Li (2.673 Å) salts. The crystallographic structures suggest influence of the alkali metal ions on the hydrogen bond network and additionally on peroxy ligands only in the K and Rb salts. However, because of complexity of this interaction, no correlation with respect to thermal stability could be found.

Hydrogen bonds between water molecules and peroxy group affects simultaneous liberation of water and oxygen (stage two). Breaking of hydrogen bonds destabilizes the VO(O₂)₂ fragment, leading to oxygen liberation accompanied by transfer of two electrons between peroxy groups, via vanadium. This electron transfer is also affected by the presence of the alkali metal cations. In the structure, the alkali metals are placed near (ca. 3 Å) the vanadyl oxygen atom, although they influence also the hydrogen bond network and additionally K and Rb have the ability to polarise the peroxy groups.

The polarisation effect of alkali metal ion can be clearly seen by comparing DTG peaks of K and Rb salts. Both complexes are isomorphous, therefore effect of the hydrogen bond network on the stability should be the same. The observed difference in the peak position (143 C for K and 107 C for Rb) is caused by their different polarising powers (which is higher for K).

Main solid product of the thermal decomposition is MVO₃ (M = Li, Na, K, Rb, Cs) as evidenced by the presence of bands in the FT-IR spectra (in KBr, cm⁻¹): 962, ~916 (sh), 841, ~660 (sh), 481 (which corresponds well with the literature data [27] for α-NaVO₃ (cm⁻¹): ν(VO₂)_{sym} 962, 916, 828; ν(VOV)_{asym} 651; ν(VOV)_{sym} 482). Small differences in the positions of the bands between our and literature data can be explained by small differences in their polymorphic forms.

However, the colour of the residue after heating to 550 C was grey or black suggesting formation of small amounts of byproducts. The analysis of the residue by e.s.r. method gave a spectra (example is given in Fig. 6) with a single resonance centred around g = 1.96 (Fig. 6) with no hyperfine structure. These spectra are characteristic for magnetically interacting V⁴⁺ centres which are close enough (dimer, cluster) to cause a dipolar broadening of the e.s.r. line [28]. The same spectrum we obtained for VO₂ (99.9% Aldrich) suggesting that tetravalent vanadium should likely be present as a VO₂ in the residue obtained (in our TG experiments) after heating the peroxocomplexes to 550 C under argon.

Quantitative estimation using vanadyl sulphate as a reference sample indicated about 8 ± 2% of total vanadium in +4 oxidation state.

The experimental mass loss is higher than the one calculated assuming MVO₃ as the only product. On the other hand the increased mass loss and formation of grey/black residue can be explained by alternative reaction:

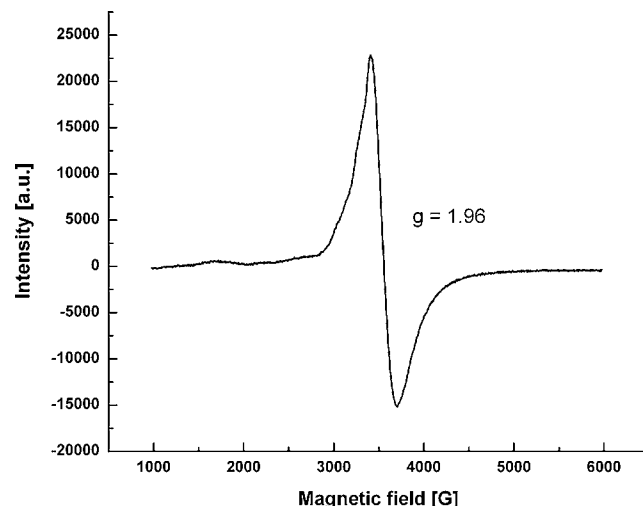
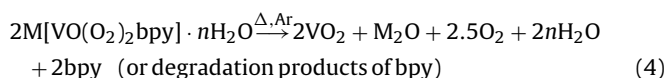


Fig. 6. Exemplary e.s.r. spectrum for the decomposition product of NabpV.

4. Conclusions

Three stages were observed during thermal decomposition of the complexes. In the first stage (dehydration) 2–4 water molecules are released and the positions of DTG peaks depend on the strength of the weakest bond in the hydrogen bond network (which is also influenced by the alkali metal ion). Water release disrupts the hydrogen bonds which stabilized the peroxy groups. Therefore in the second stage both water and oxygen molecules are released. In the case of K and Rb salts the peroxy groups are also stabilized by the alkali metal ion through polarisation effect. In the third stage 2,2'-bpy and its decomposition products are released.

The most stable is the Cs[VO(O₂)₂bpy]·H₂O₂ complex in which the lattice water molecule was substituted by H₂O₂. In the first stage hydrogen peroxide undergoes decomposition to water and molecular oxygen. Following stages are similar to hydrated complexes.

The main component of the residue is proper vanadate, MVO₃, with small amounts of paramagnetic vanadium(IV) species, most likely VO₂.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.tca.2010.11.029.

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