Thermal decomposition of potassium μ-oxo- and μ-hydroxo-bis(oxo-diperoxovanadate)

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In the thermal decomposition of vanadates $K_4[V_2O_3(O_2)_4] \cdot 2H_2O$ and $K_3[HV_2O_3(O_2)_4] \cdot H_2O$ in air, the decomposition intermediates react with carbon dioxide present in air. The decomposition products of both peroxo complexes are KVO_3 and $K_3[VO(O_2)_2CO_3]$.

При термическом разложении ванадатов $K_4[V_2O_3(O_2)_4] \cdot 2H_2O$ и $K_3[HV_2O_3(O_2)_4] \cdot H_2O$ на воздухе имеет место реакция промежуточных продуктов разложения с оксидом CO_2 воздуха. Продуктами разложения данных пероксидных комплексов являются KVO_3 и $K_3[VO(O_2)_2CO_3]$.

Up to the present, the thermal properties of oxo-peroxo-vanadates were investigated mainly by dynamic methods. The DTA and TG curves of $Na_3[V(O_2)_4] \cdot aq$ [1], $K_4[V_2O_3(O_2)_4] \cdot aq$ [1], $KVO_5 \cdot 1/2H_2O$ [2, 3], $KVO_4 \cdot 1/2H_2O$ [3], and $K_2H_2V_2O_{10} \cdot 1/2H_2O$ [3, 4]* indicate one-step liberation of peroxidic oxygen which manifests itself by a conspicuous exothermic maximum in the temperature region 50—150°C. Because of a considerable amount of heat released during the decomposition of peroxo compounds, a dynamic method appears to be poorly suited for investigating the progress of decomposition reactions.

In the scope of systematic study of slow decomposition of the vanadium(V) peroxo compounds, we investigated in this study the products of thermal reactions of $K_4[V_2O_3(O_2)_4] \cdot 2H_2O$ and $K_3[HV_2O_3(O_2)_4] \cdot H_2O$ under conditions which did not allow a rapid liberation of peroxidic oxygen.

Experimental

Preparation of substances

μ-Oxo-bis(oxo-diperoxovanadates) $M_4^I[V_2O_3(O_2)_4] \cdot xH_2O$ were for the first time prepared by *Melikov* and *Pisarzhevskii* [6] and μ-hydroxo-bis(oxo-diperoxovanadates)

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* The composition of the compound is certainly incorrect, it must be $K_3[HV_2O_3(O_2)_4]$ or a mixture of several substances [5].

$M_3^I[HV_2O_3(O_2)_4] \cdot xH_2O$ were for the first time obtained by *Wieghardt* and *Quilitsch* [7] and independently by us using different procedure [5].

$K_4[V_2O_3(O_2)_4] \cdot 2H_2O$: 0.69 g KVO_3 (5 mmol) was dissolved in 20 ml of H_2O and 5 ml of 1 M-KOH and 3 ml of 30% H_2O_2 were added into the solution.

The yellow solution thus formed was mixed with 50 ml of ethanol. The bright yellow precipitate which arose was washed with ethanol and ether. The substance was relatively stable at laboratory temperature. After five months, its weight decreased by 0.63%, but the infrared spectrum did not change.

$K_3[HV_2O_3(O_2)_4] \cdot H_2O$: 0.69 g KVO_3 was dissolved in 2.5 ml of hot 1 M-KOH. After cooling, 2 ml of 30% H_2O_2 were added into the solution. The crystallization at laboratory temperature gave lemon-yellow crystals which were after three days separated and washed with cold water and ethanol. The weight and infrared spectrum of $K_3[HV_2O_3(O_2)_4] \cdot H_2O$ did not change after five months standing under laboratory conditions.

Analyses

Potassium was determined by flame photometry, vanadium(V) by titration with iron(II) sulfate and peroxidic oxygen manganometrically with potentiometric indication.

For $K_4[V_2O_3(O_2)_4] \cdot 2H_2O$ calculated: 33.25% K, 21.66% V, 27.21% O_2^{2-}; found: 33.01% K, 21.61% V, 26.87% O_2^{2-}.

For $K_3[HV_2O_3(O_2)_4] \cdot H_2O$ calculated: 28.31% K, 24.60% V, 30.90% O_2^{2-}; found: 28.12% K, 24.78% V, 30.31% O_2^{2-}.

Thermal decomposition

The thermal decomposition was observed in static air atmosphere in a drying oven for 95 days at 76 ±2°C. The temperature which was chosen according to the DTA and TG curves below the initial temperature of exothermic effect appeared to be too low. For accelerating the decomposition, the temperature was raised to 96 ± 2°C and the decomposition was observed for subsequent 44 days. As the aim of investigation was to determine the products of thermal reactions which were identical at both temperatures used, this temperature increase did not affect the results obtained. The course of thermal reactions was traced by means of weight loss, chemical analysis of the solid products, infrared spectroscopy, and X-ray diffraction patterns.
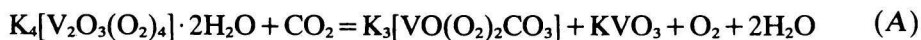
The infrared spectra were measured on an instrument Spectromaster (Grubb Parsons) within the range 4000—400 cm^{-1} in Nujol suspension. The X-ray diffraction patterns were taken with a diffractometer Philips equipped with a goniometer PW 1058, radiation CuK_α.

Results and discussion

The weight loss accompanying the thermal decomposition of $K_4[V_2O_3(O_2)_4] \cdot 2H_2O$ and $K_3[HV_2O_3(O_2)_4] \cdot H_2O$ was smaller than it should be according to the

loss of peroxidic oxygen found by chemical analysis. The explanation of this unexpected phenomenon was made possible by infrared spectra. The bands of KVO_3 and an unknown carbonate complex with a bidentate CO_3^{2-} group were identified in the spectra of the products of thermal decomposition. This result stimulated the synthesis of pure carbonate complex of vanadium(V). The complex with the composition $K_3[VO(O_2)_2CO_3]$ [8] was prepared from aqueous solution. This complex had the characteristics (infrared spectrum, X-ray diffraction pattern) identical with those of the carbonate complex present in the mixture of decomposition products.

The rate of thermal decomposition of both substances at temperatures below 100°C is dependent on many factors (air humidity, content of CO_2 in air, sample surface, *etc.*). However, the carbonate complex always arises independently of the decomposition rate and the stoichiometry of decomposition is given by the following equations

$$K_4[V_2O_3(O_2)_4] \cdot 2H_2O + CO_2 = K_3[VO(O_2)_2CO_3] + KVO_3 + O_2 + 2H_2O \qquad (A)$$

$$2K_3[HV_2O_3(O_2)_4] \cdot H_2O + CO_2 = K_3[VO(O_2)_2CO_3] + 3KVO_3 + 3O_2 + 3H_2O \quad (B)$$

Figs. 1 and 2 represent the successive changes in infrared spectra during thermal decomposition. The final products KVO_3 and $K_3[VO(O_2)_2CO_3]$ appear in the mixture after the first days of thermal decomposition. The bands of KVO_3 as well as carbonate complex are clearly visible in the spectra of both substances after 37 days' decomposition (Fig. 1, curve *b*; Fig. 2, curve *b*). Furthermore, only a few bands which correspond neither to reactants nor to final products are to be observed in the spectra. These bands may be assigned to reaction intermediates (in Figs. 1 and 2 these bands are designated by *M*). The decomposition of $K_4[V_2O_3(O_2)_4] \cdot 2H_2O$ was finished after 139 days. Only the bands of KVO_3 and $K_3[VO(O_2)_2CO_3]$ appear in the infrared spectrum (Fig. 1, curve *c*). The X-ray diffraction pattern and chemical analysis of the mixture of products are consistent with that fact. Calculated according to eqn (*A*): 22.83% V, 14.34% O_2^{2-}; found: 22.72% V, 14.32% O_2^{2-}. The products of $K_3[HV_2O_3(O_2)_4] \cdot H_2O$ decomposition contain small amounts of the decomposition intermediates even after 139 days' decomposition (Fig. 2, curve *c*). This is also betokened by chemical analysis. Calculated according to eqn (*B*): 28.20% V, 8.86% O_2^{2-}; found by analysis of the product mixture: 27.86% V, 9.84% O_2^{2-}.

$K_4[V_2O_3(O_2)_4] \cdot 2H_2O$ and $K_3[HV_2O_3(O_2)_4] \cdot H_2O$ are stable at laboratory temperature. The reaction of peroxo complexes with carbon dioxide sets in after partial
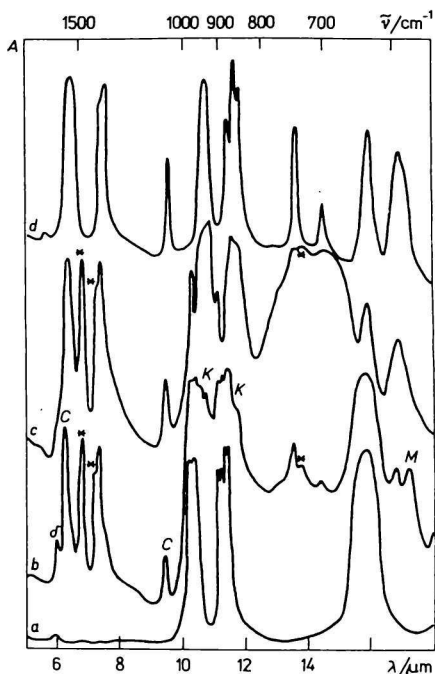
Fig. 1. Infrared spectra of $K_4[V_2O_3(O_2)_4] \cdot 2H_2O$ and products of its decomposition.

a) $K_4[V_2O_3(O_2)_4] \cdot 2H_2O$; b) after 37 days' decomposition; c) after 139 days' decomposition; d) $K_3[VO(O_2)_2CO_3]$.
K — KVO_3; C — $K_3[VO(O_2)_2CO_3]$;
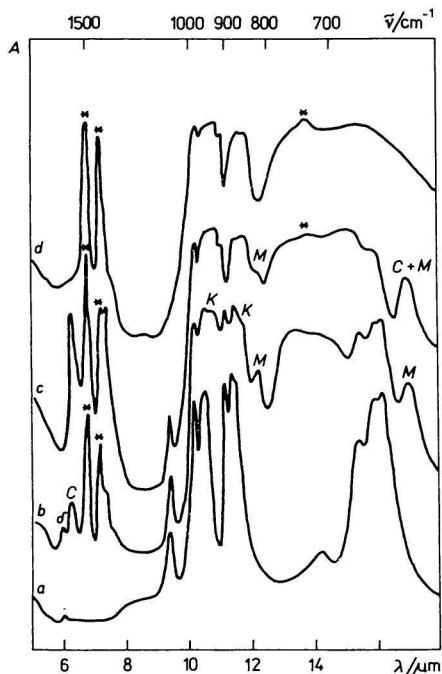M — intermediates; * — Nujol; δ — δ(H_2O).

Fig. 2. Infrared spectra of $K_3[HV_2O_3(O_2)_4] \cdot H_2O$ and products of its decomposition.

a) $K_3[HV_2O_3(O_2)_4] \cdot H_2O$; b) after 37 days' decomposition; c) after 139 days' decomposition; d) KVO_3.
K — KVO_3, C — $K_3[VO(O_2)_2CO_3]$;
M — intermediates; * — Nujol; δ — δ(H_2O).

liberation of the peroxidic oxygen, which means that the decomposition intermediates react. Though the results are not sufficient for describing the total course of decomposition, they enable us to make some assumptions about the pertinent processes.

The characteristic coordination number of the vanadium(V) peroxo complexes is 7 and the minimum coordination number is 6 [8]. After the loss of peroxidic oxygen (which may be liberated either with preservation or breaking of the O—O bond) the complex becomes unsaturated as regards coordination. For completing the coordination polyhedron, mainly the following possibilities come into consideration: a) Linkage of H_2O into coordination sphere. This process may be

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accompanied by the transfer of a proton from water to other oxygen atom. b) Binding of CO_2 from air.* c) Polycondensation reactions due to the presence of the terminal OH groups.

As the monomeric $K_3[VO(O_2)_2CO_3]$ and polymeric KVO_3 (containing chains of tetrahedrons) are reaction products, all three types of reaction are likely to take place in the course of thermal decomposition. The molecules of H_2O and OH groups must certainly play an important role in these reactions. According to infrared spectra, both substances lose their crystal water in the course of a few days of decomposition. However, the band $\delta(H_2O)$ appears again in the spectrum in the later stage of decomposition (Fig. 1, curve b and Fig. 2, curve b), which is evidently due to binding of the H_2O molecules from air.

The formation of the monomeric $K_3[VO(O_2)_2CO_3]$ necessitates splitting of the dimeric ion $[V_2O_3(O_2)_4]^{4-}$ or $[HV_2O_3(O_2)_4]^{3-}$ into two fragments. The fragments containing two peroxo groups are able to form carbonate complex in the reaction with CO_2 while the fragments with one or without any peroxo group can successively form the polymeric ion $(VO_3)_n^{n-}$ and simultaneously release the excess peroxidic oxygen. The latter process is the essence of the thermal decomposition of $K[VO(O_2)_2H_2O]$ yielding KVO_3 [10].

References

1. Grigoryeva, N. K. and Dergacheva, K. N., *Izv. Akad. Nauk SSSR, Ser. Khim. 6*, 943 (1962).
2. Vorobyeva, N. A. and Bogdanov, G. A., *Zh. Fiz. Khim. 48*, 1420 (1974).
3. Vorobyeva, N. A., Bogdanov, G. A., and Jurchenko, G. K., *Izv. Vyssh. Ucheb. Zaved., Khim. Khim. Tekhnol. 13*, 1242 (1970).
4. Vorobyeva, N. A. and Bogdanov, G. A., *Zh. Fiz. Khim. 47*, 1967 (1973).
5. Úškert, D., *Thesis.* Komenský University, Bratislava, 1979.
6. Melikov, P. G. and Pisarzhevskii, L. V., cited in *Tr. Inst. Khim. Ural. Nauch. Cent. Akad. Nauk SSSR 24*, 151 (1971).
7. Wieghardt, K. and Quilitsch, U., *Z. Naturforsch. 34B*, 242 (1979).
8. Schwendt, P., Petrovič, P., and Úškert, D., *Z. Anorg. Allg. Chem. 466*, 232 (1980).
9. Churchill, M. R., Harris, G. M., Lashewycz, R. A., Dasgupta, T. P., and Koshy, K., *Inorg. Chem. 18*, 2290 (1979).
10. Schwendt, P. and Joniaková, D., to be published.

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* CO_2 is likely to combine with the OH group, which gives temporary existence to the HCO_3 group. For the Co(III) complexes, it has appeared that mainly the terminal OH group and not the bridge OH group [9] is able to react with CO_2.