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THERMAL DECOMPOSITION OF OXOPEROXOOXALATO COMPLEXES OF VANADIUM /V/

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ABSTRACT

Products of the isothermal and nonisothermal (up to 250°C) decomposition of $K_3[VO(O_2)_2C_2O_4]$ and $K_3[VO(O_2)_2C_2O_4] \cdot H_2O_2$ have been studied by means of X-ray phase analysis and IR spectroscopy. The release of the peroxo oxygen from anhydrous complex is a one-step process. Decomposition of the perhydrate proceeds in three steps. The oxygen (from H_2O_2) and a half of water content is released in the first two steps and a stable intermediate $K_3[VO(O_2)_2C_2O_4] \cdot 0.5H_2O$ is thus formed. In the third step, all peroxo oxygen (from the coordinated O_2 groups) and the remaining water, are released. The final products of decomposition in both cases are KVO_3 and $K_2C_2O_4$.

INTRODUCTION

In the course of the thermal decomposition of vanadium /V/ peroxo complexes after partial loss of the peroxo oxygen, coordinatively unsaturated intermediate products,are formed. Mutual reactions of these intermediates and their reactions with molecules from the surrounding atmosphere result in the formation of various decomposition products. Decomposition processes were studied mostly in the case of vanadium /V/ peroxo complexes with monodentate ligands (F, H_2O, NH_3)[1-5]. This contribution deals with the decomposition of vanadium /V/ peroxo complexes with a bidentate oxalato group.

EXPERIMENTAL

The complexes $K_3[VO(O_2)_2C_2O_4]$(I)[6] and $K_3[VO(O_2)_2C_2O_4] \cdot H_2O_2$ (II)[7] were prepared according to the published methods.

The thermoanalytical curves were registered in the temperature range 25 - 250 °C, in a static air atmosphere with the help of derivatograph (system: F. Paulik, J. Paulik, L. Erdey, MOM Budapest).

The isothermal decomposition was investigated in a static

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air atmosphere for 120 days at 124 ± 3 °C (I) and for 29 days at 120 ± 3 °C (II). The course of the thermal reactions was followed according to weight loss, by means of elemental analyses of solid intermediate products, infrared spectroscopy (Specord 75 IR) and X-ray powder patterns (Philips diffractometer PW 1058, Cu K_α radiation). The samples were investigated after cooling down to room temperature.

RESULTS AND DISCUSSION

The complexes $K_3[VO(O_2)_2C_2O_4]$ and $K_3[VO(O_2)_2C_2O_4]\cdot H_2O_2$ are relatively stable, they decompose at temperatures above 100 °C.

The DTA, TG and DTG curves for $K_3[VO(O_2)_2C_2O_4]$ are shown in Fig. 1. The only step on the TG curve which was accompanied by a strong exothermic peak on the DTA curve with a maximum at 210 °C, corresponds to the loss of all peroxo oxygen. The final product of thermal decomposition of $K_3[VO(O_2)_2C_2O_4]$ up to 250 °C was a mixture of KVO_3 and $K_2C_2O_4$. In the course of the isothermal decomposition, the formation of stable intermediate products, were not observed. The reaction mixture contained $K_3[VO(O_2)_2C_2O_4]$, KVO_3 and $K_2C_2O_4$ during decomposition. The weight loss, chemical analysis, IR spectrum and X-ray pattern confirmed that the final products of isothermal decomposition were KVO_3 and $K_2C_2O_4$ (calcd. for 1:1 mixture of KVO_3 and $K_2C_2O_4$: weight loss 9.52%, 16.74% V, 28.92% $C_2O_4^{2-}$, found : weight loss 10.13%, 16.81% V, 27.85% $C_2O_4^{2-}$). The stoichiometry of decomposition is given by equation (1):

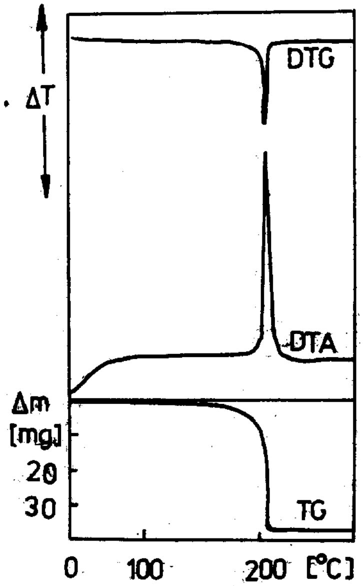

Fig. 1. DTA, TG and DTG curves for $K_3[VO(O_2)_2C_2O_4]$ (m= 300 mg, b,25 °C/min)

$$K_3[VO(O_2)_2C_2O_4] = KVO_3 + K_2C_2O_4 + O_2 \qquad (1)$$

As it can be seen from the DTG curve (Fig. 2) the decomposition of $K_3[VO(O_2)_2C_2O_4] \cdot H_2O_2$ is a three-step process. The weight loss in the first two steps corresponds to the loss of peroxo oxygen from H_2O_2 (calcd. 4.32%, found 4.25%) and to the following release of half of water molecules (calcd. 2.43%, found 2.10%). On the DTA curve these reactions are expressed by a weak exothermic and the ensuing endothermic effects. By interrupting of thermal analysis at 162 °C, a stable intermediate with the composition $K_3[VO(O_2)_2C_2O_4] \cdot 0.5H_2O$, was obtained (calcd. 18.53% O_2^{2-} , 14.76% V, 6.95% C, 0.29% H, found 18.39% O_2^{2-}, 14.19% V, 6.61% C, 0.42% H). The third step on the DTG curve accompanied by a strong exothermic peak on the DTA curve, corresponds to the loss of all remaining peroxo oxygen and water (weight loss calcd. 11.87%, found 12.25%). The decomposition stoichiometry is given by eqns. (2) and (3) :

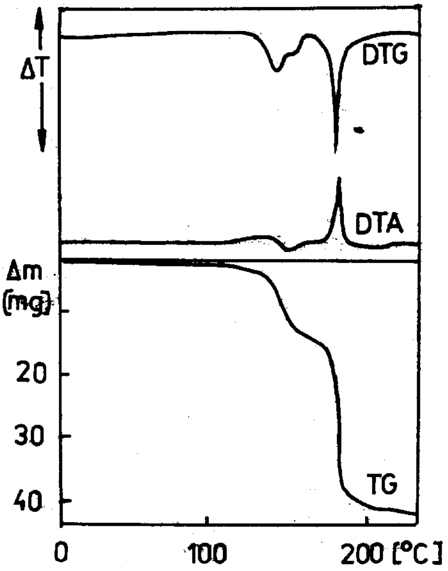

Fig. 2. DTA, TG and DTG curves for $K_3[VO(O_2)_2C_2O_4] \cdot H_2O_2$ (m= 200 mg, 1,25 °C/min)

$$K_3[VO(O_2)_2C_2O_4] \cdot H_2O_2 = K_3[VO(O_2)_2C_2O_4] \cdot 0.5H_2O + 0.5H_2O + 0.5\,O_2 \qquad (2)$$

$$K_3[VO(O_2)_2C_2O_4] \cdot 0.5H_2O = KVO_3 + K_2C_2O_4 + O_2 + 0.5H_2O \qquad (3)$$

The results obtained by the isothermal study are analogous. The gradual decrease of intensity of bands at 3550 cm^{-1} and 870 cm^{-1}, which correspond to vibrations of H_2O_2 in perhydrates [7], can be observed in the IR spectra of solid samples taken during the thermal decomposition.

The obtained intermediate product $K_3[VO(O_2)_2C_2O_4].0.5H_2O$ differs in its characteristics from all known oxoperoxooxalatovanadates /V/. The IR spectrum of this compound indicates some changes in the coordination of the oxalato ligand in comparison with $K_3[VO(O_2)_2C_2O_4].H_2O_2$.

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