ACTIVATION ENERGY OF THE THERMAL DECOMPOSITION OF AMMONIUM METAVANADATE. A THERMOGRAVIMETRIC STUDY

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The thermogravimetric curves of the title compound (AMV), recorded at two rates of heating (10 and 1.25 deg min⁻¹), exhibited two separate steps of weight loss (at 423-513 and 513-613 K). The TG curves were analysed by testing 18 solid-state reaction equations associated with the methods of Coats and Redfern (1964), Šatava and Škvára (1969) and Blazejowski et al. (1983). On the basis of linearization procedures, high-order reactions with n = 1.5 and 2.0 best described the two TG steps. The activation energies of the two conversion stages are: first stage: 163.6 and 152.6 kJ mol⁻¹, and second stage: 238.1 and 167.7 kJ mol⁻¹ (low and high heating rates, respectively).

The overall reaction for the thermal decomposition of ammonium metavananate (AMV) is generally represented as

$$2 \text{NH}_4\text{VO}_3 \rightarrow \text{V}_2\text{O}_5 + 2 \text{NH}_3 + \text{H}_2\text{O}$$

accompanied by a total weight loss of 22.2% of the original sample weight. The decomposition does not take place in a single stage, but in several stages, and there is still little agreement as to the intermediates formed, the results depending on the method of detection and characterization. The mass losses after particular stages led some earlier investigators [1, 2] to believe that HVO₃ is one of the products. A three-stage decomposition was suggested to occur in air or oxidizing atmospheres by Brown et al. [3–5]:

$$\text{AMV} \xrightarrow{423-453 \text{ K}} \text{ABV (ammonium bivanadate)} \xrightarrow{453-483 \text{ K}} \text{AHV}$$

(ammonium hexavanadate) \xrightarrow{533-573 \text{ K}} \text{V}_2\text{O}_5.$$

The formations of the intermediates are atmosphere-dependent stages. This was supplemented by differential enthalpic analysis (DEA) and IR spectroscopy [6].
Formation of the hexavanadate intermediate was confirmed by Sas et al. [7]. A series of intermediates \( (M_1-M_4) \) were detected by X-ray and IR techniques by Furuichi et al. [8] in thermal decompositions performed in different atmospheres. The decomposition of AMV to \( V_2O_5 \) was conceived by Kunaev et al. [9] to proceed through stages involving the release of \( \text{NH}_3 \) and \( H_2O \), but with the formation of intermediate solids different from those mentioned above. A completely different mechanism was proposed by Kalicki et al. [10], in which \( H_2O \) and \( \text{NH}_3 \) are released at 373–423 K, \( \text{N}_2 \), NO and \( N_2O \) at 423–473 K, and the remaining \( \text{NH}_3 \) at 573 K. A three-stage decomposition mechanism was deduced by Dziemba et al. [11] from redox measurements. From DTA tracings recorded in different atmospheres, two and three-stage endothermic processes have also been suggested, depending on the atmosphere involved [12].

The present study reports the thermogravimetry of AMV performed at two widely differing rates of heating in order to detect the possible separate appearance of the various decomposition processes. The TG curves are rigorously analysed with respect to the predominant decomposition mechanism and the associated activation energies.

**Experimental**

**Material**

Analytical grade ammonium metavanadate (B.D.H.) was analysed at two heating rates by means of two apparatuses. At the high rate of heating of 10 deg min \(^{-1}\), analysis was carried out with an MOM apparatus (Hungary). At the low heating rate of 1.25 deg min \(^{-1}\), a thermobalance produced by Gebrunder Netzsch, West Germany, was used. The obtained recordings are presented in Fig. 1.

![Fig. 1 Thermogravimetric curves of ammonium metavanadate, recorded at different heating rates](image)