Thermochimica Acta, 235 (1994) 99–103
Elsevier Science B.V., Amsterdam
SSDI 0040-6031(93)01484-K

Evolved gas analysis during the thermal decomposition of $(NH_4)_4V_2O_{11}$ in an inert atmosphere

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(Received 26 May 1993; accepted 5 July 1993)

Abstract

Mass spectroscopic results confirm that water vapour, ammonia and oxygen are the main gas products that form during the thermal decomposition of $(NH_4)_4V_2O_{11}$. From the results it is clear that the decomposition consists of a number of steps which overlap. The mass spectroscopic results fit the results as observed by thermogravimetry. From 60°C, when a heating rate of $2°C\,min^{-1}$ is used, the compound loses a molecule of water to form $NH_4[VO(O_2)_2(NH_3)]$, which decomposes in the next step into $NH_4[VO_3(NH_3)]$ (from 85°C). The decomposition rate of the first reaction is slower than that of the second reaction. From 125°C (heating rate $2°C\,min^{-1}$), $NH_4[VO_3(NH_3)]$ decomposes into ammonium metavanadate. This reaction seems to consist of two steps, and could include temperature-dependent mechanisms.

INTRODUCTION

In a previous paper [1] it was proposed that although the reaction products of some of the decomposition reactions are unstable at the reaction temperatures, $(NH_4)_4V_2O_{11}$ decomposes to $(NH_4)[VO(O_2)_2(NH_3)]$ at 93°C, which seems to decompose to $(NH_4)[VO_3(NH_3)]$ at 106°C and then to ammonium metavandate at 145°C when a heating rate of $2°C\,min^{-1}$ is used. NH_4VO_3 decomposes through several steps to vanadium pentoxide [2–5]. It was shown that the reaction temperature ranges overlap even on going down to heating rates of $0.1°C\,min^{-1}$. Above 320°C, vanadium pentoxide is formed. However, only the mass loss curves during heating of the sample and some infrared spectroscopic results have been investigated. Therefore, it was decided to identify the gas-phase decomposition products and to confirm the proposed decomposition steps by means of evolved gas analysis.

EXPERIMENTAL

A Shimadzu TG/MS instrument was used to collect mass spectroscopic data of the gases evolved during the heating of the compound using a

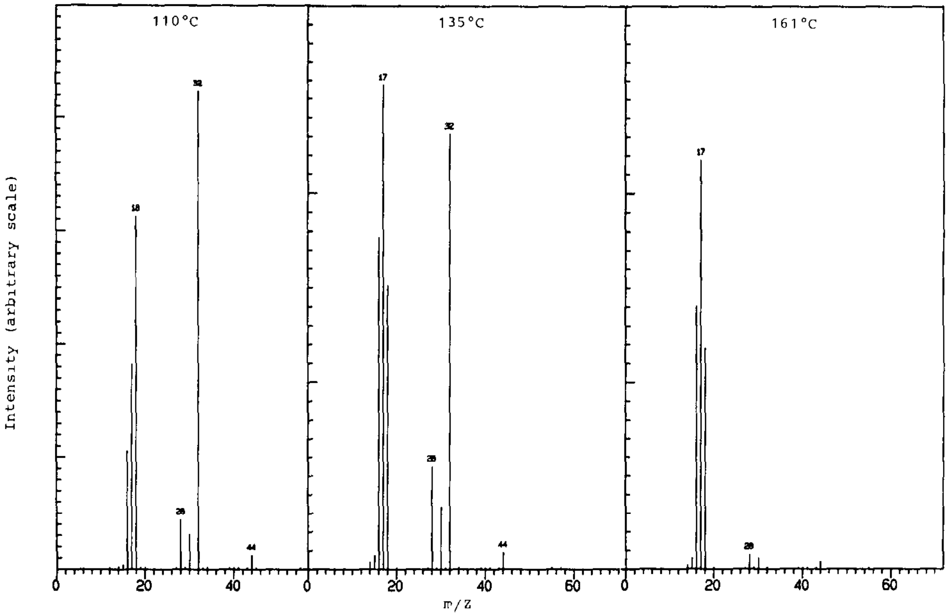

Fig. 1. Mass spectra of the gases evolved at 110, 135 and 161°C.

heating rate of 2°C min^{-1}. A helium atmosphere with a flow rate of approximately 50 cm^3 min^{-1} was used and sample masses were approximately 5 mg. Prior to heating, the sample was subjected to helium flow (using the same flow rate as for the analysis) for 12 h in the instrument in order to eliminate oxygen from the atmosphere. The sample was kept at room temperature. $(NH_4)_4V_2O_{11}$ was prepared and characterized as described in a previous paper [1].

RESULTS AND DISCUSSION

Figure 1 shows the mass spectra of the gases evolved at 110, 135 and 161°C. The peaks at masses of 18 and 32 are solely due to the presence of H_2O and O_2 in the gas decomposition phase. The peak at a mass of 17 amu has a contribution (OH^+) from the water vapour peak (23% of peak at mass 18 [2]) and from NH_3 in the decomposition gases. The relatively high peak at a mass of 16 also indicates that some ammonia is present, because the NH_2^+ part (mass 16) of NH_3 (mass 17) would give a peak with 80% of the height of the NH_3 peak [2]. Peak height ratios between the peaks at masses of 17 and 18 are 0.6 at 110°C, 1.7 at 135°C, and 1.8 at 161°C. These ratios and the presence of high peaks at a mass of 32 amu at 110 and 135°C, indicate that at 110°C, O_2 and H_2O are the main gas-phase decomposition products. Small amounts of ammonia are also detected. At 135°C, NH_3 and H_2O are the main gas-phase decomposition products, while the amount of oxygen formed, although still present, is greatly reduced. No oxygen is

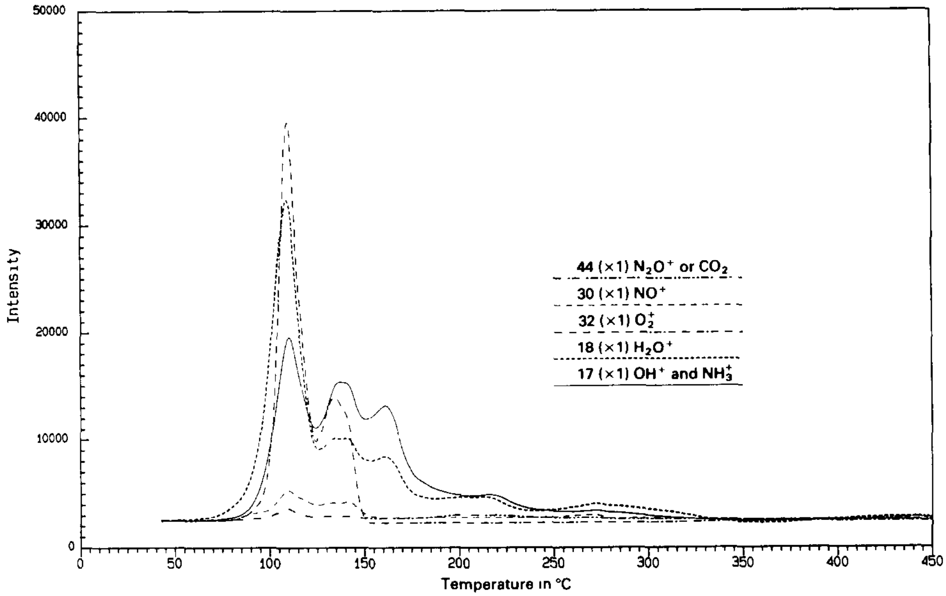

Fig. 2. Mass spectroscopic single-ion intensity curves for the gases H_2O, O_2 and NH_3 from 50 to 450°C.

observed at 161°C and the decomposition gases are ammonia and water vapour.

The very weak peaks at a mass-to-charge ratio of 12 indicate that very little carbon or carbon-related species are present, as expected for a compound that does not contain carbon. Small peaks at 28 and 44 amu indicate the presence of CO and CO_2, which are often produced by the carbon in the filament of the ion source of the instrument, or by impurities in the filament or compound under investigation [2]. The carbon (usually carbide) reacts with any oxygen or water vapour to form CO and CO_2. CO is commonly the second major constituent of any mass spectrometry system and peaks at 28 and 44 amu are expected [6]. The peak at a mass of 28 amu can also include a contribution from N_2^+ as rearrangement of the nitrogen atoms from NH_3 can occur to a small extent. The peak at a mass of 30 amu seems to be due to NO^+ which can be produced by the presence of water vapour and ammonia in the analysing chamber. For the same reason, an N_2O^+ peak at 44 can appear on the spectra.

Figure 2 gives the MS single-ion intensity curves for the gases H_2O, O_2 and NH_3 from 50 to 450°C. From Fig. 2, it is clear that the first gas that is formed is H_2O, from approximately 60°C. Water vapour is given off throughout the reaction with the greatest amount being evolved between 60 and 125°C. It is only from approximately 350°C that no water vapour is given off. At about 85°C, oxygen starts to be indicated on the spectrum. The temperature of 88°C, chosen as the upper limit for the isothermal decomposition studies for the kinetics of the first process [1], seems to fall well within the limits as the second process would only just have started at that temperature. The O_2^+ MS peak is very strong at about 110°C and a second much lower intensity peak is observed with a maximum at approximately 135°C. No oxygen is formed at temperatures exceeding 150°C.

Unfortunately, the OH^+ and NH_3^+ peaks both have a mass number of 17 and are, therefore, overlapping. The first peak with a maximum at 110°C is much lower than the H_2O^+ peak and well underneath it. This would be largely due to OH^+ ion from water vapour. The second and third peaks with mass number 17 are much higher than the water vapour peak at a mass number of 18, and thus could not be due to water vapour alone. The second and third mass-17 peaks with maximum heights at approximately 140 and 160°C must therefore be due to the presence of NH_3^+ and H_2O^+ ions.

CONCLUSIONS

It is apparent from the mass spectroscopic results that the decomposition reactions of ammonium peroxovanadate overlap to a great extent. Nevertheless, the mass spectroscopic results fit the decomposition process [1] that can be summarized as following (heating rate 2°C $\min^{-1}$)

$$>60°\text{C} \quad (NH_4)_4V_2O_{11}(s) \rightarrow 2NH_4[VO(O_2)_2(NH_3)](s) + H_2O(g) \qquad (1)$$

$$>85°\text{C} \quad NH_4[VO(O_2)_2(NH_3)](s) \rightarrow NH_4[VO_3(NH_3)](s) + O_2(g) \qquad (2)$$

$$>125°\text{C} \quad NH_4[VO_3(NH_3)](s) \rightarrow NH_4VO_3(s) + NH_3(g) \qquad (3)$$

$$>150°\text{C} \quad 2NH_4VO_3(s) \rightarrow V_2O_5(s) + 2NH_3(g) + H_2O(g) \qquad (4)$$

The last reaction occurs via a number of intermediate products.

Using the peak widths on Fig. 2 as an indication of reaction rate, it seems that reaction (1) is slower than reaction (2). The two NH_3 peaks at mass 17 above 125°C indicate that reaction (3) consists of two steps or that two temperature-dependent decomposition mechanisms may be involved.

ACKNOWLEDGEMENTS

The author thanks Mr Y. Takai of the Materials Characterization Laboratory of the Torary Research Centre in Shiga, Japan, for performing the analysis and also Dr M. Todoki from the same laboratory for all his assistance in organizing the analysis.

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