Journal of Thermal Analysis, Vol. 2 (1970) 287–299

THE THERMAL DECOMPOSITION OF AMMONIUM METAVANADATE, I

THE STOICHIOMETRY OF THE DECOMPOSITION

M. E. Brown and B. V. Stewart

Chemistry Department, Rhodes University, Grahamstown, South Africa

(Received March 14, 1970)

The stoichiometry of the various stages involved in the thermal decomposition of ammonium metavanadate has been shown to correspond to a stepwise decrease in the ratio of ammonia and water to V_2O_5, with V_2O_5 being the final product in vacuum, in air and in argon. In ammonia, VO_2 is formed. The actual stages and intermediates are dependent upon the prevailing atmosphere. Chemical analyses, together with infrared absorption spectra and X-ray powder data, have enabled the intermediates and products to be characterized and the structural changes involved in the decomposition to be discussed.

The overall reaction for the thermal decomposition of ammonium metavanadate (AMV) is believed to be

$$2\,NH_4VO_3 \rightarrow V_2O_5 + 2\,NH_3 + H_2O \qquad (1)$$

This corresponds to a total loss of 22.2% of the original sample mass.

The decomposition does not, however, occur in a single stage, but in several stages and there is little agreement on the intermediates formed. This disagreement stems from several factors. The intermediates are very dependent upon the conditions of temperature and surrounding atmosphere during the decomposition and, under certain conditions, the ammonia formed may be oxidized or catalytically decomposed by the vanadium pentoxide, giving products other than those in reaction (1). Several investigators have used only the mass-loss during a particular stage to characterize the intermediates and have been misled into believing HVO_3 to be one of the products [1, 2]. Taniguchi and Ingraham [5] have pointed out that several possible reactions, leading to different intermediates, can give almost the same mass losses and they suggested the use of the ratio of the amounts of ammonia and water evolved as the factor determining the stoichiometry.

Most of the studies of the thermal decomposition of AMV [1–6] have been dynamic thermal analyses and little attempt has been made to obtain the detailed kinetic and mechanistic information available when working under isothermal conditions. An exception to this is the work of Deschanvres and Nouet [7] arising out of their study of the preparation of oxygen bronzes of vanadium and ammonia [8]. They studied the kinetics of the first stage of the decomposition only. This stage takes place at ca. 180° and was represented as

$$6\,NH_4VO_3 \rightarrow (NH_4)_2V_6O_{16} + 4\,NH_3 + 2\,H_2O \qquad (2$$

which corresponds to a loss of 14.8% of the original sample mass. The solid product has the empirical formula of ammonium hexavanadate (often represented as the "trivanadate" $NH_4V_3O_8$).

Trau [3, 4], from the results of a TG study in air, concluded that an intermediate corresponding to $(NH_4)_2V_4O_{11}$, ammonium "bivanadate", is formed with a mass-loss of 11.1% at lower temperatures (<180°); this decomposes in turn (<210°) to give the hexavanadate

$$4\,NH_4VO_3 \rightarrow (NH_4)_2V_4O_{11} + 2\,NH_3 + H_2O \qquad (3)$$

$$3\,(NH_4)_2V_4O_{11} \rightarrow 2\,(NH_4)_2V_6O_{16} + 2\,NH_3 + H_2O \qquad (4)$$

Finally, above 300 °C

$$(NH_4)_2V_6O_{16} \rightarrow 3\,V_2O_5 + 2\,NH_3 + H_2O \qquad (5)$$

Lamure and Colin [9] found that the bivanadate is only formed with small sample masses, slow heating rates and rapid removal of product gases.

The hydrated form of the bivanadate, $(NH_4)_2V_4O_{11} \cdot 3\,H_2O$, has been prepared as a precipitate obtained on boiling an aqueous AMV solution [10] or by adding ethanol to the cooled solution after boiling and filtering [11]. Attempts to obtain the anhydrous form [9] were unsuccessful, leading instead to the hexavanadate. Kelmers [12] has prepared ammonium hexavanadate from acidified AMV solution. Although ammonium hexavanadate has been proposed as a decomposition intermediate in several studies, there is some disagreement in the reported X-ray powder data for this intermediate [5, 6, 9, 12, 13].

Controversy over the nature of the final solid product of the decomposition of AMV has arisen largely from the differences in the prevailing conditions of temperature and surrounding atmosphere. V_2O_5 is thought to be formed first, but if the gaseous products (NH_3, H_2O) are allowed to accumulate in large samples, or in the presence of atmospheres of reducing gases (NH_3 or H_2), lower oxides may be formed [14, 15]; e.g., when AMV is heated in a stream of ammonia, at temperatures ranging from 500° to 1500°, the products are very dependent upon the temperature [16, 17]; at 500° V_2O_3 is the main solid product, but above 600° the product has the VN lattice incorporating oxygen in amounts which decrease as the temperature increases. All the VN prepared in this way contains some residual oxygen incorporated in the lattice.

This lack of agreement on the stages involved in the thermal decomposition of ammonium metavanadate, together with an interest in the conversion of ammonium metavanadate to vanadium nitride [18], led to a re-investigation of the reaction.

The DTA traces of Erdey et al. [1] and Taniguchi and Ingraham [5] indicated that the decomposition of AMV is an endothermic process. Endothermic decompositions [19, 20] usually show some degree of reversibility and hence the results of a study of the decomposition in hard vacuum, where recombination reactions are minimized, are of importance. The decomposition in vacuum is considerably different to the decomposition in the various gases at atmospheric pressure, and the stages involved have not previously been well characterized.

Experimental

Isothermal gravimetric analyses on powder samples (12 ± 0.1 mg) of AMV were carried out using a Cahn RG vacuum electrobalance and a micro furnace. Sample temperatures were calibrated by the Curie point method [21]. Powder samples from several manufacturers gave similar results.

Attempts to obtain suitable single crystals according to the method of Lukesh [22] were unsuccessful. Deschanvres and Nouet [7] have reported that when larger single crystals were prepared, these tended to break up at the start of the decomposition into small crystals with dimensions and decomposition kinetics similar to the material before recrystallization.

Analyses

Nitrogen was determined by a standard micro-Kjeldahl method. The percentage vanadium was calculated directly from the initial composition of AMV and the mass loss for the particular stage, assuming no vanadium loss. The calculation of the empirical formulae of the intermediates is based, as far as possible, on the mass-spectrometric evidence of Deschanvres and Nouet [7] that, at least in the earlier stages of the decomposition, ammonia and water are evolved in the mole ratio of 2 : 1.

Discrepancies between the observed and expected nitrogen content (Table 1) may arise from the small samples used in the N-analyses and the possibility of adsorption on the reactive surfaces of partially decomposed material. There is also the possibility that the stages are not completely separated and that the intermediates and products may be non-stoichiometric on account of defects formed during decomposition [6].

The samples used for the analyses were the combined products of several replicate decompositions, for the maximum sample mass used in a particular run was limited by the dimensions of the bucket and furnace. It was deemed undesirable to use different heating conditions, e.g. a larger furnace, for preparation of samples for analysis as, on account of self-cooling, these samples could then not be accurately correlated with those prepared on a small scale; Lamure and Colin [9] have demonstrated that the nature of the products obtained is dependent on the sample mass.

Table 1

The thermal decomposition of ammonium metavanadate

Stage	Temp. range, °C	Empirical formula of product	Mass loss (%)		Nitrogen (%)	
In vacuum			ex-pected	measured	ex-pected	found
1	105—135	$NH_4V_3O_8$ or $(NH_4)_2O \cdot 3\ V_2O_5$ (A)	14.83	14.5—14.7	4.68	4.77
2	135—155	$NH_4V_4O_{10.5}$ or $(NH_4)_2O \cdot 4\ V_2O_5$	16.66	16.9—17.2	3.59	3.48
3	165—200	V_2O_5	22.23	22.3—22.6	0	0
In air						
1	160—180	$(NH_4)_2V_4O_{11}$ or $(NH_4)_2O \cdot 2\ V_2O_5$	11.10	11.7—11.8	6.74	6.82
2	180—210	$NH_4V_3O_8$ or $(NH_4)_2O \cdot 3\ V_2O_5$ (B)	14.83	15.6—15.9	4.68	4.44
3	260—300	V_2O_5	22.23	22.3—22.4	0	0
In argon						
1	160—180	$(NH_4)_2V_4O_{11}$ or $(NH_4)_2O \cdot 2\ V_2O_5$	11.10	11.7—11.8	6.74	6.82
2	180—210	$NH_4V_3O_8$ or $(NH_4)_2O \cdot 3\ V_2O_5$ (C)	14.83	15.9—16.0	4.68	4.45
3	270—300	V_2O_5	22.23	22.3—22.4	0	0
In ammonia						
1	170—190	$NH_4V_3O_8$ or $(NH_4)_2O \cdot 3\ V_2O_5$ (D)	14.83	14.6—14.8	4.68	4.27
2	280—300	$NH_4V_6O_{15}$ or $(NH_4)_2O \cdot 2\ VO_2 \cdot 5\ V_2O_5$	19.95	19.9	2.48	2.63
3	340—360	VO_2	29.05	28.2—28.4	0	0

Results

The decomposition of AMV was studied under isothermal conditions at various temperatures, both with continuous removal of the products by evacuation, and in atmospheres of argon (inert), air (oxidizing), and ammonia (reducing). Under all of these conditions the decomposition takes place in several successive stages. The total mass-losses, the temperature ranges which give conveniently measurable rates of decomposition, and the suggested empirical formulae of the products of each stage are given in Table 1. At the higher temperature ends of the temperature ranges given in Table 1, some overlap of stages tended to occur. The ends of such stages were judged from the results at the lower temperature ends of the ranges, where constant, reproducible mass-losses were obtained.

Identification of the solid products

From Table 1, on the basis of empirical formulae only, the solid products of the 1st stage in vacuum (A), the 2nd stage in air (B), the 2nd stage in argon (C) and the first stage in ammonia (D), are all similar. X-ray powder diffraction data and infrared spectra in KBr matrix show that B, C and D are the same compound, but that the structure of the intermediate A, although it also has the empirical formula $NH_4V_3O_8$, does not correspond to that of intermediates B, C and D.

The infrared spectra and X-ray powder data of B, C and D correspond to that of the compound precipitated from acidified ammonium metavanadate solution according to the method of Kelmers [12]. The X-ray powder data differs from those of Satava [6] and of Taniguchi and Ingraham [5] for their intermediates of empirical formula $NH_4V_3O_8$, but Lamure and Colin [9] report that the data for their intermediate was in agreement with that given by Kelmers [12].

The final product of the decomposition in vacuum, air and argon is V_2O_5. The broad infrared bands and the high background and decreased detail in the X-ray powder photographs of the final product in vacuum as compared to the product in air and in argon indicate that this material is a more defective form of V_2O_5. Some of this disorder appears to anneal on heating in air, at about 350°, giving an improved spectrum and X-ray powder photograph, with no detectable change in mass.

Discussion

The stages found for the decomposition in air, using isothermal measurements, are in excellent agreement with the TG results in air, using small samples and slow heating rates, obtained by Trau [3, 4], and are in overall agreement with the assumption that, throughout the reaction, two molecules of ammonia are evolved to every one molecule of water.

The structural changes involved in reaction (1), the decomposition of ammonium metavanadate to V_2O_5 are considerable. Firstly, no structure is yet known in which a discrete 'metavanadate' ion (VO_3^-) can be distinguished [23]. In NH_4VO_3 [19] (and KVO_3) two of the four oxygen atoms tetrahedrally surrounding each V atom are involved in linking the tetrahedra together (V – O bond-length 1.81 Å), while the other two oxygen atoms are not shared (V – O bond-length 1.66 Å). [Pure tetrahedral co-ordination occurs in the orthovanadates, $(VO_4)^{3-}$, with V – O bond-length ca. 1.66 Å.] In the hydrated metavanadates e.g., $KVO_3 \cdot H_2O$ [24], the V atoms are 5-co-ordinated in a distorted trigonal bipyramid [25], with the K^+ and H_2O occupying the interstices. Linking of this trigonal-bipyramidal arrangement into layers through oxygen gives the V_2O_5 structure [26].

The next nearest O neighbour in V_2O_5 is in the adjacent layer at a distance of 2.81 Å and can be regarded as forming a very distorted octahedron. These VO_6 octahedra form a three-dimensional framework structure [25].

Ammonium hexavanadate ($NH_4V_3O_8$) is isostructural with KV_3O_8 and CsV_3O_8 [12], whose structure has been shown [27] to consist of layers of highly distorted VO_6 octahedra linked together by sharing corners and edges, with the cations occupying positions between the layers, in irregular 12-fold co-ordination with the neighbouring oxygen atoms. The sodium and lithium analogues cannot be prepared and it is believed that the layer structure requires the presence of relatively large interlayer cations to be stable [27].

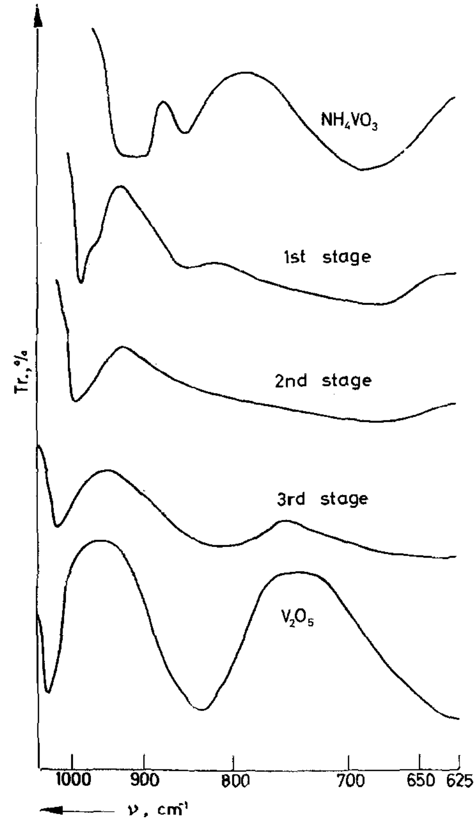

Fig. 1. Changes in V—O infrared absorption bands during decomposition in vacuum

The changes then, in going from a chain structure to a cage structure, via possibly a layer structure, should be shown up, to some extent at least, in the infrared spectra at various stages of the decomposition.

The NH_4^+ ion has two infrared active fundamental frequencies: ν_3 (N—H stretching) near 3200 cm^{-1}, and ν_4 (NH_4 deformation) near 1400 cm^{-1}. Both are triply degenerate in the freely rotating ion. In addition bands may occur in the 3000–3100 cm^{-1} region [28] and the first harmonic of ν_4, $2\nu_4$ at 2800 cm^{-1} is often detectable. Interaction of ν_4 with the torsional oscillation ν_6 of the ammonium ion on its lattice site can give rise to a band in the 1600–2000 cm^{-1} region.

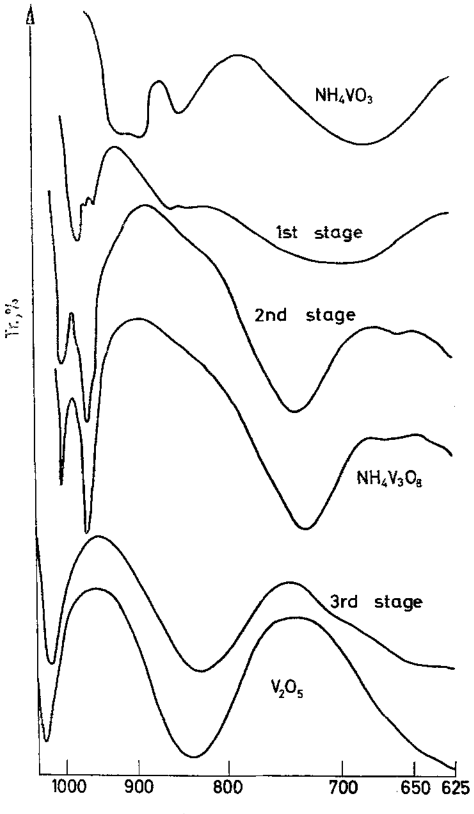

Fig. 2. Changes in V—O infrared absorption bands during decomposition in air and in argon

The V–O bands observable in the AMV spectrum in the region 1000–625 cm^{-1} are all broad. There is a band at 890 cm^{-1} with a broad shoulder on the high wavenumber side, one at 850 cm^{-1} and a very broad band centred at approximately 685 cm^{-1}. Further bands for AMV have been reported in the CsBr region at 505 cm^{-1} and 330 cm^{-1} [29]. These bands are characteristic of metavanadates containing tetrahedral chains [30]. Bands in the region 950–850 cm^{-1} are attributed to the stretching frequencies of the shorter (unshared) V–O bonds, while bands around 700 cm^{-1} and 550 cm^{-1} are characteristic of V–O–V chains.

The band at 1020 cm^{-1} in the infrared spectrum of V_2O_5 has been attributed [31] to the V=O stretching vibration and the broad band at 825 cm^{-1} represents the stretching vibration of the V–O–V group in the lattice layer corresponding to the (010) plane in V_2O_5.

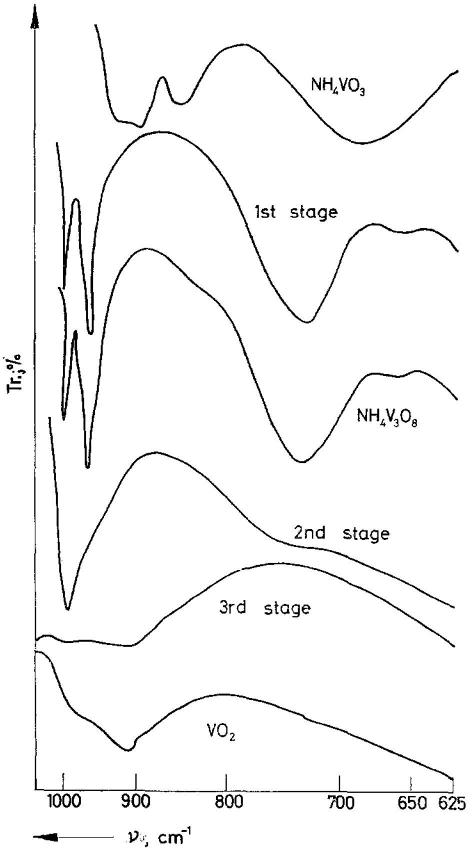

Fig. 3. Changes in V–O infrared absorption bands during decomposition in ammonia

The changes occurring in the V–O bands during the course of the decomposition are illustrated in Fig. 1 (decomposition in vacuum), Fig. 2 (decomposition in air and in argon) and Fig. 3 (decomposition in ammonia).

The following changes occur in the ammonium bands. The first stage of the decomposition in vacuum and in air and in argon results in products which have a satellite band on the high wavenumber side of the ν_4 ammonium vibration at 1400 cm^{-1}. This satellite band persists through the second stage of the decomposition in vacuum, although its intensity decreases and, by half-way through the third stage in vacuum, the satellite band is detectable only as a slight shoulder on the main band. The final process is the removal of the last traces of ammonium ion from a basically V_2O_5 structure.

For the decomposition in air and in argon, however, the satellite band is missing in the spectra of the products of the second stage as well as in the spectrum of the product of the complete first stage of the decomposition in ammonia. These spectra correspond to that of the ammonium hexavanadate preparation [12].

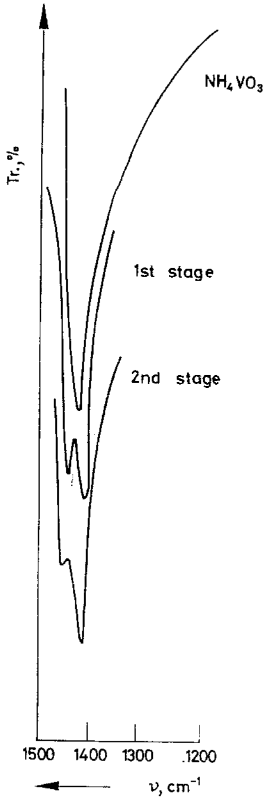

Fig. 4. Changes in the main ammonium infrared absorption band during the various stages of the decomposition in vacuum

The changes in the ammonium band during the various stages of the decomposition in vacuum are shown in Fig. 4. The satellite band was found to develop only during the last fraction ($\alpha > 0.75$) of the first stage of the decomposition in vacuum.

A similar satellite band on the high wavenumber side of the ν_4 band at 1400 cm^{-1} has been reported in several studies of the infrared spectra of ammonium salts [28, 32–38]. Two interpretations have been put forward for the presence of this band: the symmetry of the NH_4^+ ion environment has been decreased either through the occurrence of an order–disorder transition, or through restriction of the originally free rotation of the NH_4^+ ion, generally through hydrogen-bonding. Neutron spectrometric experiments [33, 34] on ammonium halides seem to favour the former explanation, as they indicate that the ammonium ion does not rotate freely in the simple ammonium halide salts, although it has been pointed out [39] that the possibility of free rotation of the NH_4^+ ion is enhanced by the increase in the uniformity of the crystalline field in salts with high lattice symmetry containing polyatomic anions of low charge.

Waddington's criteria [28] for hydrogen-bonding in NH_4^+ salts, in addition to the splitting of the 1400 cm^{-1} band, include similar splitting of the 3000 cm^{-1} band, and the appearance of the $\nu_4 + \nu_6$ interaction band near 1700 cm^{-1}. Interpretation in the region of the 3000 cm^{-1} band is complicated by the $2\nu_4$ overtone and the $\nu_4 + \nu_2$ combination (3000–3100 cm^{-1}) as well as the water bands which are difficult to eliminate when using a KBr matrix. Waddington does note that the asymmetry of the environment of the NH_4^+ ion may be sufficient to remove the degeneracy of the ν_3 and ν_4 modes.

Miller and Wilkins [40] pointed out that in their survey of the infrared spectra of a large number of ammonium salts (at room temperature) no splitting of the NH_4^+ bands was detected, even in substances which would be expected to display strong hydrogen-bonding.

The splitting that has been detected, has been in the low temperature spectra of salts such as ammonium chloride [32, 36] and ammonium dichromate [35] where there is evidence of order–disorder transitions. To the authors' knowledge splitting of the NH_4^+ bands in the spectra of intermediates in the thermal decomposition of ammonium salts has not been reported before.

If it is assumed that the presence of the satellite NH_4^+ band near 1440 cm^{-1} in the infrared spectrum of an intermediate indicates a disordered structure, in terms of the NH_4^+ ion arrangement, then some such disordered structure is formed during the first stage of the decomposition in vacuum, and in air, and in argon.

This disordered state must be formed by a combination of random removal of NH_4^+ ions from the structure with lowering of the symmetry of the NH_4^+ ion environment by changes in the V–O structure, as the oxygen involved in the formation of the H_2O is derived from the V–O network. The poorly defined V–O bands in the infrared spectra of these intermediates support this view.

The X-ray powder photographs of the products of the 1st and 2nd stages in vacuum are very similar and this, together with the constancy of the V–O bands in the IR spectra, indicates that the changes during decomposition are occurring within a basically unaltered V–O framework.

The ordered arrangement of NH_4^+ ions is never restored and the final product is a defective form of V_2O_5.

$$(NH_4)_2O \cdot V_2O_5 \rightarrow \underset{\text{(disordered structure)}}{(NH_4)_2O \cdot 3\,V_2O_5} \rightarrow$$

$$\underset{\text{(disordered)}}{(NH_4)_2O \cdot 4\,V_2O_5} \rightarrow \underset{\text{(disordered)}}{V_2O_5}$$

The intermediate formed during the second stage of the decomposition in air and in argon is similar to the product of the first stage of the decomposition in ammonia, and to ammonium hexavanadate AHV prepared from solution. The single NH_4^+ band in the infrared spectra of these compounds indicates an ordered arrangement of NH_4^+ ions in the structure. This ordered intermediate decomposes in air and in argon to give V_2O_5.

The second stage of the decomposition in ammonia results in an intermediate of empirical formula $(NH_4)_2O \cdot 2\,VO_2 \cdot 5\,V_2O_5$, in agreement with the results of Satava [6].

To summarize, then, the stoichiometry of the decomposition in air and in argon is

$$(NH_4)_2O \cdot V_2O_5 \rightarrow \underset{\text{(disordered structure)}}{(NH_4)_2O \cdot 2\,V_2O_5} \rightarrow$$

$$\underset{\text{(ordered)}}{(NH_4)_2O \cdot 3\,V_2O_5} \rightarrow \underset{\text{(ordered)}}{V_2O_5}$$

while in ammonia

$$(NH_4)_2O \cdot V_2O_5 \rightarrow \underset{\text{(ordered)}}{(NH_4)_2O \cdot 3\,V_2O_5} \rightarrow$$

$$\underset{\text{(ordered)}}{(NH_4)_2O \cdot 2\,VO_2 \cdot 5\,V_2O_5} \rightarrow VO_2$$

When ammonium metavanadate is decomposed in vacuum to the end of the first stage (i.e. mass-loss of 14.6%) and, after cooling, the decomposition is then continued in air, two stages are detected: at about 220°, decomposition to a total mass-loss of 19.6% occurs and the final stage to V_2O_5 (22.4% mass-loss) takes place at about 300°. Both the AHV preparation and the product of the second stage of the decomposition in air, which has been identified as AHV, decompose to V_2O_5 in air, in single stages, which is further evidence that the product of the first stage of the decomposition in vacuum is not AHV.

On the other hand, the product of the first stage of the decomposition in air decomposes in vacuum to V_2O_5 in a single stage at about 180°. This temperature is unusually high for a decomposition stage in vacuum. It appears then that although the product of the first stage of the decomposition in air has been assumed to have a disordered structure, the presence of the air, probably through its action in inhibiting the removal of the gaseous products, has resulted in a structure which decomposes in vacuum less readily than would be expected.

Conclusions

The stoichiometry of the thermal decomposition of ammonium metavanadate (AMV) in vacuum, and in air, argon and ammonia atmospheres, has been studied. Except for the later stages of the decomposition in ammonia, the results correspond well to the gradual reduction of the ratio of "$(NH_4)_2O$" to "V_2O_5" units from the original 1 : 1 ratio in AMV, which may be written as $(NH_4)_2O \cdot \cdot V_2O_5$, to pure V_2O_5, with ammonia and water being evolved throughout the decomposition in the mole ratio of 2 : 1.

A disordered structure is formed initially under all conditions, but when the removal of the product gases is hindered, or in the presence of an excess of ammonia, further decomposition leads to an ordered intermediate, which has been shown to be the same as ammonium hexavanadate. The final product of decomposition in air, argon and in vacuum is V_2O_5 and in ammonia, below 360°, VO_2.

*

We wish to acknowledge helpful comments from Prof. L. Glasser and Dr. N. H. Agnew and financial support from the National Institute for Metallurgy, Johannesburg, South Africa.

References

1. L. Erdey, S. Gál and G. Liptay, Talanta, 11 (1964) 913.
2. C. Duval, Inorganic Thermogravimetric Analysis, Elsevier, Amsterdam, 1953, p. 170.
3. J. Trau, Roczniki Chem., 36 (1962) 1365.
4. J. Trau, Zeszyty Nauk. Politech. Krakow, 21 (1966) 113.
5. M. Taniguchi and T. R. Ingraham, Can. J. Chem., 42 (1964) 2467.
6. V. Satava, Collection Czech. Chem. Commun., 24 (1959) 2172.
7. A. Deschanvres and G. Nouet, Compt. Rend. Acad. Sci. Paris, Ser. C., 265 (1967) 2041.
8. A. Deschanvres, G. Nouet and B. Raveau, Compt. Rend. Acad. Sci. Paris, 261 (1965) 3144.
9. J. Lamure and G. Colin, Compt. Rend. Acad. Sci. Paris, 258 (1964) 6433.
10. C. Calvo, Ph. D. Thesis, Rutgers University, 1954.
11. M. Lacharte, Bull. Soc. Chim. France, 35 (1924) 321.
12. A. D. Kelmers, J. Inorg. Nucl. Chem., 21 (1961) 45.
13. K. Tamara, S. Teranshi and T. Miyarzaki, J. Chem. Soc. Japan, 55 (1952) 68.
14. T. Sata, E. Komada and Y. Ito, Kogyo Kagaku Zasshi, 71 (1968) 643.
15. T. Sata and Y. Ito, Kogyo Kagaku Zasshi, 71 (1968) 647.
16. D. A. King, Ph. D. Thesis, University of the Witwatersrand, Johannesburg, 1963, p. 110.
17. V. Epelbaum and A. Brager, Acta Physicochimica USSR, 13 (1940) 595, 600.
18. H. I. Philip, Ph. D. Thesis, Rhodes University, In preparation.
19. W. E. Garner, Chemistry of the Solid State, Butterworths, London, 1955, Chapter 8.
20. D. A. Young, Decomposition of Solids, Pergamon, London, 1966, Chapter 3.
21. Perkin-Elmer Handbook — Model UU1 Temperature Programme Control, p. 3.
22. J. S. Lukesh, Acta Cryst., 3 (1950) 476.
23. M. T. Pope and B. N. Dale, Quart. Rev., 22 (1968) 539.

24. C. L. CHRIST, J. R. CLARK and H. T. EVANS, JR., Acta Cryst., 7 (1954) 801.
25. A. F. WELLS, Structural Inorganic Chemistry, Oxford University Press, 3rd Ed., 1962, p. 686.
26. H. G. BACHMANN, F. R. AHMED and W. H. BARNES, Z. Krist., 115 (1961) 110.
27. H. T. EVANS, JR., and S. BLOCK, Inorg. Chem., 5 (1966) 1808.
28. T. WADDINGTON, J. Chem. Soc., (1958) 4340.
29. F. A. MILLER, G. L. CARLSON, F. F. BENTLEY and W. H. JONFS, Spectrochim. Acta, 16 (1960) 135.
30. T. DUPUIS and V. LORENZELLI, J. Thermal Anal., 1 (1969) 15.
31. Y. KERA and K. HIROTA, J. Phys. Chem., 73 (1968) 3133.
32. E. L. WAGNER and D. F. HORNIG, J. Chem. Phys., 18 (1950) 296, 305.
33. G. VENKATARAMAN, K. USHA DENIZ, P. K. IYENGAR, A. P. ROY and P. R. VIJAYARAGHAVAN, J. Phys. Chem. Solids, 27 (1966) 1103.
34. J. J. RUSH,. T. I. TAYLOR and W. W. HAVENS, JR., J. Chem. Phys., 37 (1962) 234.
35. C. J. H. SCHUTTE and A. M. HEYNS, Chem. Phys. Letters, 1 (1967) 487.
36. C. W. GARLAND and N. E. SCHUMAKER, J. Phys. Chem. Solids, 28 (1967) 799.
37. J. A. CAMPBELL, Spectrochim. Acta, 21 (1965) 1333.
38. W. C. HAMILTON and J. A. IBERS, Hydrogen Bonding in Solids, W. A. Benjamin, New York, 1968, p. 221.
39. E. F. WESTRUM, JR., and B. H. JUSTICE, J. Chem. Phys., 50 (1969) 5083.
40. F. A. MILLER and C. H. WILKINS, Anal. Chem., 24 (1952) 1253.

RÉSUMÉ — On montre que les différentes étapes de la décomposition thermique du métavanadate d'ammonium correspondent à la diminution progressive de l'eau et de l'ammoniac par rapport à V_2O_5; cet oxyde constitue le produit final dans le vide, dans l'air et dans l'argon. Dans l'ammoniac, c'est VO_2 qui se forme. Les étapes respectives et les intermédiaires dépendent de l'atmosphère qui prévaut. A l'aide de l'analyse chimique, des spectres d'absorption infrarouge et des données de rayons X sur poudre, on a pu caractériser les intermédiaires et les produits formés, ainsi que les changements structuraux provoqués par la décomposition.

ZUSAMMENFASSUNG — Es wurde gezeigt, daß die verschiedenen Stufen in der thermischen Zersetzung von Ammoniummetavanadat dem stufenweisen stöchiometrischen Verlust von Ammonia und Wasser entsprechen. In Vakuum, Sauerstoff und Argon ist V_2O_5, in Ammoniak VO_2 das Endprodukt. Die Zwischenprodukte der einzelnen Stufen sind von der umgebenden Gasatmosphäre abhängig. Durch chemische, infrarot- und röntgenspektroskopische Analyse gelang es, diese zu charakterisieren und so die durch die Zersetzung hervorgerufenen strukturellen Umlagerungen zu deuten.

Резюме. — Показана стехиометрия различных стадий терморaспада метаванадата аммиака, соответствующих ступенчатому уменьшению аммиака и воды в V_2O_5. В вакууме, в атмосфере воздуха и аргона конечным продуктом является V_2O_5. Определенные стадии и промежуточные продукты зависят от атмосферы. Данные химического анализа, спектров инфракрасного поглощения света и рентгенограммы дали возможность характеризовать различные продукты и превращения структуры, связанные с распадом вышеуказанного вещества.