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THE THERMAL DECOMPOSITION OF AMMONIUM METAVANADATE, III

A STRUCTURAL VIEW OF THE DECOMPOSITION MECHANISM

M. E. Brown, L. Glasser and B. V. Stewart

Chemistry Department, Rhodes University, Grahamstown, South Africa

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The kinetics and thermodynamics of the thermal decomposition of ammonium metavanadate (AMV) are combined with the structural information available for AMV, for the important decomposition intermediate, ammonium hexavanadate (AHV), and for vanadium pentoxide, the product of the decomposition in non-reducing atmospheres, to enable the atomic movements involved in the course of decomposition to be discussed in detail.

The decomposition of AMV involves scission of the V–G chains in the AMV structure (accompanied by simultaneous evolution of gaseous ammonia and water) with subsequent rearrangement and cross-linking of discrete units, based on $V_3O_8^{=}$, to form AHV. Further decomposition to V_2O_5 is a similar but less ordered process.

The thermal decomposition of ammonium metavanadate, AMV, has been studied in considerable detail. The stoichiometries of the various stages of the decomposition in vacuum and in inert, oxidising, and reducing atmospheres have been determined [1] and the intermediates have been characterized by their infrared spectra and X-ray powder diffraction data. Differential enthalpic analysis was used [2] to determine thermodynamic data for the decomposition stages, and these results have been compared with the kinetic parameters in order to discuss the possible compositions of the activated complexes for the decomposition stages [3]. Provided that no reduction of the vanadium (V) occurs, the decomposition shows a high degree of reversibility [4]. A study of the effect of variation of the partial pressures of ammonia and water vapour on the rate of the reaction:

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

has permitted a mechanism for the "recombination" to be determined [4].

The crystal structure of AMV [5–8] is known, as are the structures of the important intermediate, ammonium hexavanadate, AHV [9], and of the final, unreduced product V_2O_5 [10–14]. This structural information is combined, in this study, with the decomposition results [1–4] in an attempt to outline the mechanism of the decomposition in structural terms.

Decomposition stages

Depending on ambient conditions, AMV decomposes directly or indirectly to AHV, which then decomposes in non-reducing atmospheres to V_2O_5 [1]. Thus, in a moist ammonia atmosphere, AMV decomposes directly to AHV:

$$\underset{\text{AMV}}{3NH_4VO_3(s)} \rightarrow \underset{\text{AHV}}{NH_4V_3O_8(s)} + 2NH_3(g) + H_2O(g) \tag{2}$$

while in oxidizing and in inert atmospheres the intermediate, ammonium bivanadate, ABV, is the product of the first stage:

$$\underset{\text{AMV}}{4NH_4VO_3(s)} \rightarrow \underset{\text{ABV}}{(NH_4)_2V_4O_{11}(s)} + 2NH_3(g) + H_2O(g) \tag{3}$$

The ABV then decomposes in a second stage to AHV:

$$\underset{\text{ABV}}{3(NH_4)_2V_4O_{11}(s)} \rightarrow \underset{\text{AHV}}{4NH_4V_3O_8(s)} + 2NH_3(g) + H_2O(g) \tag{4}$$

In non-reducing atmospheres the AHV intermediates, as well as AHV prepared from solution [9], decompose to V_2O_5 in a single stage:

$$2NH_4V_3O_8(s) \rightarrow 3V_2O_5(s) + 2NH_3(g) + H_2O(g) \tag{5}$$

In general, these reactions are endothermic [2] and the overall decomposition:

$$2NH_4VO_3(s) \rightarrow V_2O_5(s) + 2NH_3(g) + H_2O(g) \tag{6}$$

is readily reversible [4].

Crystal Structures

AMV

AMV, space-group Pbcm [5–8], consists of zig-zag chains of distorted tetrahedra of oxygen about vanadium, linked by their corners and extending in the *a* direction (Fig. 1(a)). The apices of the tetrahedra in any one chain point in the same direction while the apices of the tetrahedra in adjacent chains along the *b* direction point in opposite directions (Fig. 1(b)).

There are two types of V–O bond in the chains of tetrahedra. The V–O distance for the shared O-atoms is 181 ± 1 pm, while for the unlinked O-atoms the V–O distance is 166 ± 1 pm. The V–O–V angle is 145°.

The NH_4^+ ions are irregularly surrounded by ten O-atoms at distances varying from 285 to 340 pm (Fig. 1(c)) [7]. Seven V-to-O vectors are shown, while three more with the magnitudes of A, C and G have been omitted. Corresponding sets of O-atoms have been labelled I, II and III. There are clearly several alternative hydrogen-bonded configurations of the NH_4^+ ion.

The AMV structure viewed in the *b* direction is shown in Fig. 2.

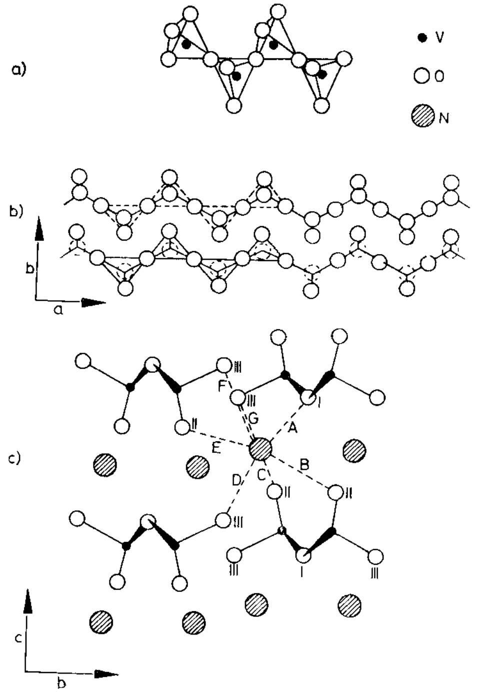


Fig. 1. Aspects of the ammonium metavanadate (AMV) structure: (a) Linking of the distorted VO_4 tetrahedra; (b) Arrangement of neighbouring chains; (c) The environment of an ammonium ion (represented by the N Atom only) viewed in the *a* direction

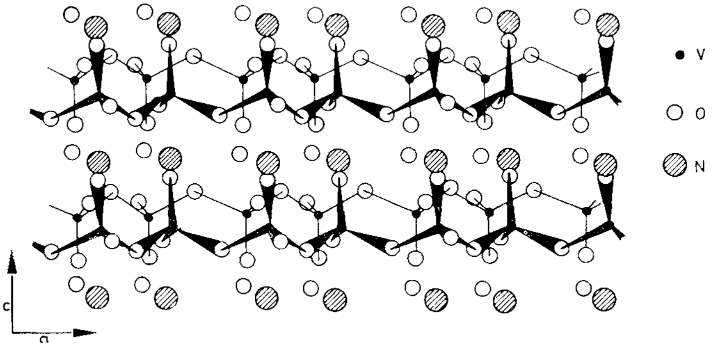


Fig. 2. The crystal structure of AMV viewed in the *b* direction, with a slight shift to show the tetrahedral arrangement with minimal superimposition

AHV

AHV [9, 10], space group $P2_1/m$, has a layer structure, based on that of $K_2V_6O_{16}$. The basic unit is a distorted VO_5 square pyramid (or, otherwise, an even more distorted VO_6 octahedron, Fig. 3(a)). Pyramids share a base edge to form V_2O_8

units, shown in idealized and distorted forms in Fig. 3(b). These units, in turn, are linked into zig-zag chains in the *b*-direction by sharing corners O_{II}, marked with arrows in Fig. 3(c). These chains are further linked, in the *c*-direction, into sheets by VO groups represented by triangles in Fig. 3(c). This V_I-O_I distance is equal to the apical $V-O$ distance in the square pyramids.

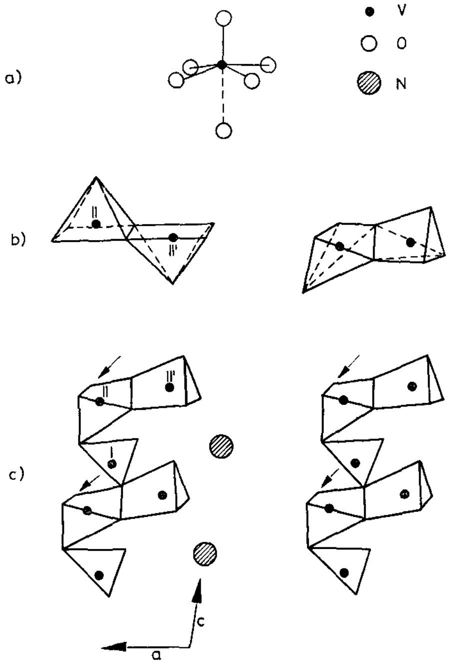


Fig. 3. Aspects of the ammonium hexavanadate (AHV) structure: (a) The basic square pyramid (inclusion of the next nearest O gives a distorted octahedron); (b) Two views of the sharing of a base edge to give a V_2O_8 group: idealized (left) and distorted as well as rotated (right); (c) The V_2O_8 groups are linked into zig-zag chains in the *b* direction by sharing the corners (O_{II}) marked with arrows. Chains are linked, in the *c* direction, into sheets by the V_I-O_I groups (triangles in projection)

The AHV structure viewed in the *a*-direction is shown in Fig. 4, with representative V_I, V_{II} and O_I, O_{II} atoms labelled to correspond with Fig. 3.

V_2O_5

The V_2O_5 structure, space group Pmnm [11–14], is built up of the V_2O_8 units represented in Fig. 3(b), linked through a third base-corner of the square pyramids into chains in the *a* direction, Fig. 5, and into layers parallel to (010) through the remaining base-corner. The six O-atoms marked to VI in the lower part of Fig. 5

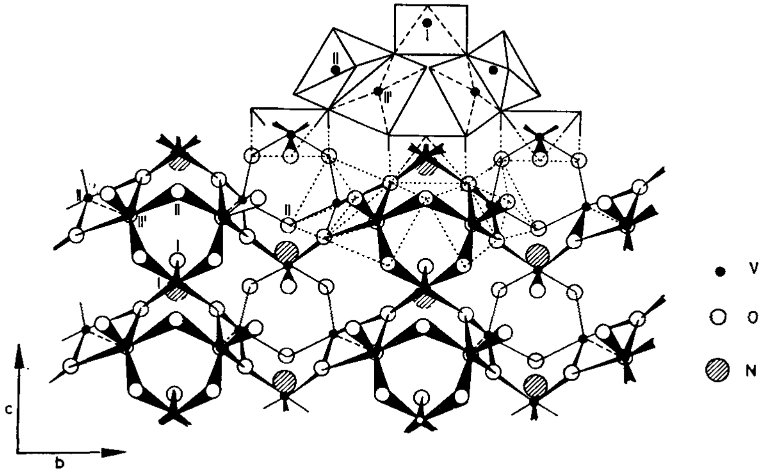


Fig. 4. The crystal structure of AHV viewed in the *a* direction. The linked square pyramids are shown in dotted outline in the main structure and extended (solid and dashed lines) to illustrate the relationship to Fig. 9(b)

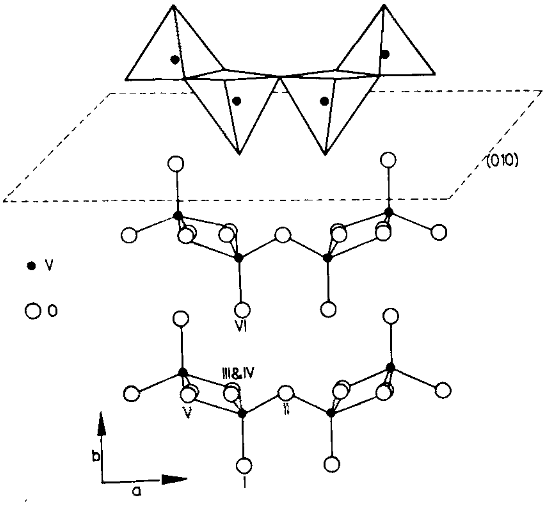


Fig. 5. The crystal structure of V_2O_5 projected on (001), (superimposed oxygens have been symmetrically displaced). The top row shows the linking of the square pyramids. The six-fold co-ordination of vanadium by oxygen atoms, labelled I to VI, is also shown

may alternatively be regarded as lying in distorted octahedral co-ordination about V, but the V-to-O_{VI} distance is large (281 pm) compared to the other V–O distances of from 154 to 202 pm.

ABV

Even though the detailed crystal structure of ABV has not, to the authors' knowledge, been determined, useful information on its properties is available [15–17].

ABV is relatively soluble in water compared to AMV, AHV and V_2O_5. The greater solubility of the ABV intermediate suggests that the structure of ABV is unlikely to consist of extensively interlinked groups of vanadium and oxygen atoms, as in AMV and AHV, but rather of discrete ionic $(V_4O_{11})_n^{2-}$ units, where *n* is some small integer. The hydrated form of ABV, $(NH_4)_2V_4O_{11} \cdot 3H_2O$, has been prepared from solution [15, 16] but attempts at dehydration led to decomposition to AHV [17].

The infrared spectrum [1] of the ABV intermediate indicates that the environment of the NH_4^+ ions is asymmetrical since there is no degeneracy of the symmetrical bending mode of the NH_4^+ ion at about 1400 cm^{-1}.

The Decomposition Mechanism

The structures of the solid reactants, decomposition intermediates and final products of the thermal decomposition of AMV are closely related. Electron microscopy shows that during the complete course of decomposition the external structure of the reactant crystallites is little altered [3]. The surface roughening which does occur is uniform and not associated with original surface defects.

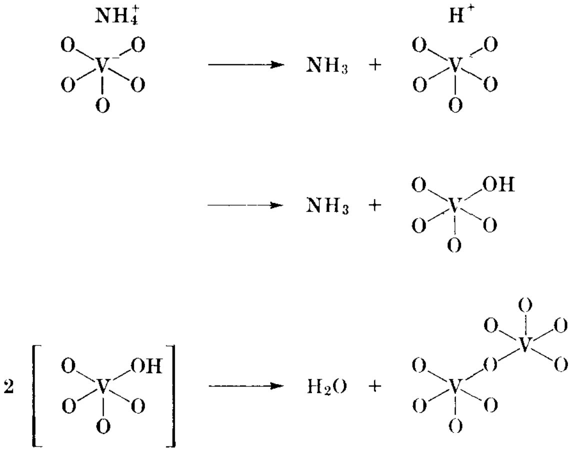
The peaks in the differential enthalpic analyses [2] all correspond to endothermic processes and the changes in X-ray powder diffraction patterns and in the V–O infrared absorption bands [1] of not only the intermediate products of the AMV decomposition stages, but also of the partially decomposed solid reactant at intervals during decomposition stages, are all continuous, with no indication of distinct re-crystallization processes.

The decomposition intermediates ABV and AHV, as well as the final product V_2O_5, react readily with damp ammonia to re-form AMV. These recombinations all take place in single, diffusion-controlled stages [4]. The general shape and size of the crystallites are retained through decomposition and recombination [3, 4] and this, together with the evidence against recrystallization suggests that there are no profound changes in the basic structure of the material. The removal and re-admission of gaseous products appears to be from a basically little altered V–O framework.

We have not been able to determine the detailed crystallographic orientation of the product or intermediate phases relative to that of the AMV crystallites. Such information would establish whether the reaction was topotactic or at least epitactic [18]. Even in principle this would be difficult because of the motion of the reactant/product interface from the surface to the centre of the crystallites according to the contracting-envelope model [3].

Using Schmidt's dictum [19, 20] that "reaction in the solid state occurs with a minimum amount of atomic or molecular movement" it is possible to propose a decomposition mechanism.

The first step in the decomposition involves the breaking of the distorted tetrahedral VO_4 chains of AMV into discrete units. Although ABV can only be isolated as an intermediate in non-reducing atmospheres, it is suggested that the same basic process occurs in all atmospheres. The stoichiometry of reaction (2) requires that these units should be based on a ratio of three vanadium to eight oxygen atoms. Making the assumption that fracture of the VO_4 chains is a co-operative process, yielding identical V_3O_8 units, and choosing the positions of fracture in AMV to allow the formation of AHV with the minimum of atomic movement, yields the situation illustrated in Fig. 6, which is derived directly from Fig. 2, with the omission of two molecules of ammonia and one of water for every three "molecules" of AMV, as is appropriate for the decomposition. The detailed mechanism for the evolution of ammonia and water, throughout the decomposition, may be expected to be rather similar to that proposed for the thermal decomposition of ammonium-exchanged zeolites [21–23], viz:



For the ammonium-exchanged zeolites similar steps have been shown to be readily reversible [21] as is the case for the AMV decomposition [4].

Each of the V_3O_8 units formed (Fig. 6) may be considered to rotate (about an axis joining the two terminal vanadium atoms (V_{II})) away from the direction in which the apices of the tetrahedra point, through 135° or 45° alternately. This process is accompanied by a contraction in the *b* and *c* directions of AMV, resulting in the orientation of these units shown in Fig. 7. These units then cross-link to form the AHV structure (Fig. 4).

This whole process is probably best visualized by following the re-arrangements of the V–O polyhedra. The VO_4 chains in AMV, Fig. 8(a), defined from Fig. 2, break at the points marked with the arrows, on removal of the oxygen as water. The V_3O_8 fragments may then rotate as in Fig. 8(b) to give the configuration shown in Fig. 8(c).

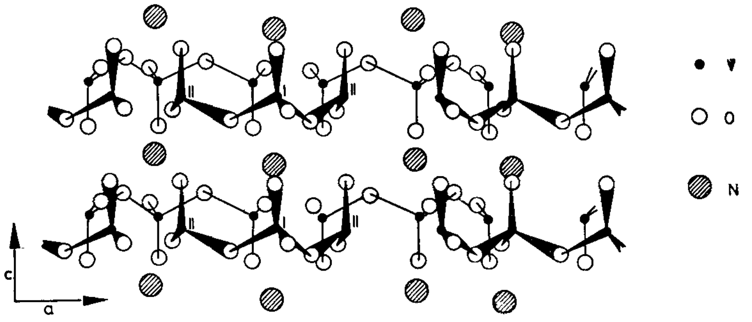


Fig. 6. The breaking of the distorted tetrahedral VO_4 chain of AMV (viewed along the *b* direction) during decomposition to AHV

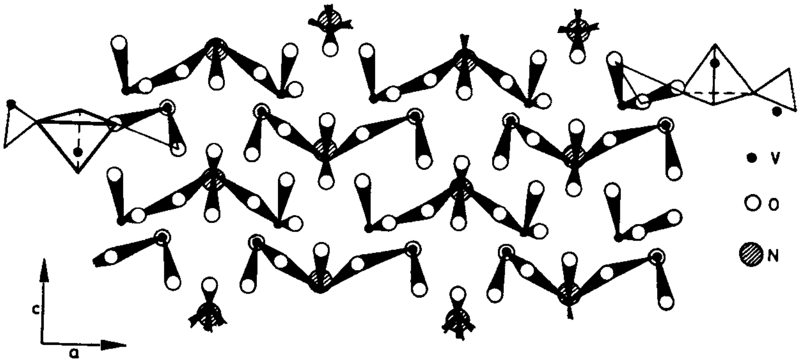


Fig. 7. The arrangement of V_3O_8 units, after rotation and contraction in the *c* and *b* directions, but prior to cross-linking to form AHV. The outlines of the tetrahedra and fragments are given to illustrate the relationship to Fig. 8(c)

By redefinition of the polyhedra as shown in Fig. 9(a) one arrives at the AHV structure of Fig. 4 with the linked square-pyramids outlined, Fig. 9(b).

It should be noted that the structures have been slightly distorted in drawing to emphasize the perspective.

The isolation of the ABV intermediate under certain conditions [1] suggests that scission of the V—O chains in AMV into discrete units is largely complete in these conditions before cross-linking (to AHV) occurs. Then, at the higher temperatures needed for the decomposition of ABV, the movements required for the cross-linking to AHV will be facilitated. However, during decomposition in an ammonia atmosphere, where ABV is not isolated, the evolution of the gaseous products is impeded and the temperatures required to give decomposition rates equivalent to those in inert and oxidizing atmospheres are slightly higher [1]; motion then occurs more readily, and chain scission may be followed immediately by some cross-linking to AHV.

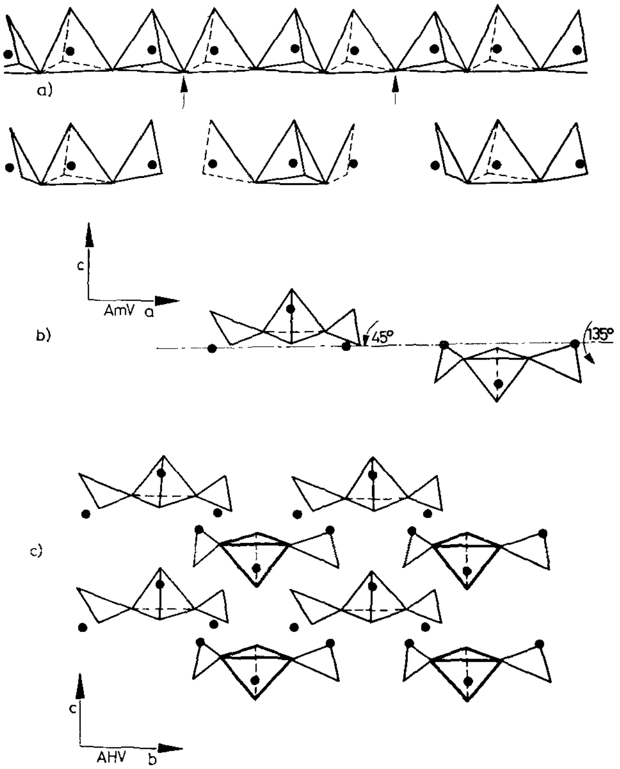


Fig. 8. The first steps in the decomposition of AMV: (a) A tetrahedral VO_4 chain in AMV. Arrows mark the point of removal of oxygen, to give V_3O_8 units in their original orientation, in the second row; (b) The two orientations of the V_3O_8 units after rotation about the axis through the terminal (V_{II}) vanadium atoms, and contraction in the *b* and *c* directions of AMV; (c) Two reoriented fragments from each of four VO_4 chains, forming a $2 \times 2 \times 2$ arrangement in the *a*, *b* and *c* directions shown in projection as viewed in the *a* direction of AHV (or the *b* direction of AMV)

Note: Slight shifts have been made to improve the perspective by reducing superimposition. The heavy lines outline the tetrahedra in the foreground.

A chain scission process, as suggested, into ideally $V_3O_8^-$ units will, undoubtedly, lead to some disordered regions, and these will be minimized if conditions allow a certain degree of reversibility of the decomposition process e.g., if the gaseous products are not rapidly removed. The decomposition intermediate AHV* [1] formed during decomposition in vacuum has a less ordered structure than AHV.

Models based on various types of thermal decomposition processes in simple linear polymers [24–26] e.g., the largely structure-controlled dehydrochlorination of poly(vinylidene chloride), (PVDC), and the dehydration of poly(methyl vinyl ketone), (PMVK), to cross-linked carbons, although not based on chain scission, do involve decomposition at points along the chain followed by cross-linking, and give rise to deceleratory α-time curves which are not inconsistent with the application of the contracting volume equation to the AMV decomposition [3]. The dehydrochlorination of PVDC [26], for example, takes place in two stages via an essentially polyene structure. This is thought to be formed in a "zip" reaction [24] and shows first-order kinetics, while cross-linking in the second stage is via a Diels–Alder mechanism.

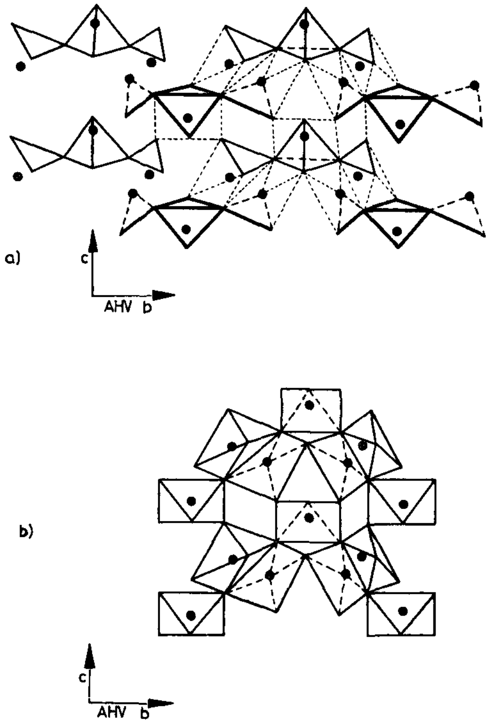


Fig. 9. (a) Redefinition of the V—O polyhedra of Fig. 8(c), to give; (b) The conventional representation of the AHV structure (cf. Fig. 4) in terms of linked square pyramids. Solid lines within the outlines of the polyhedra, lie above the plane of the square and dashed lines below. The double square pyramids are linked by V_I—O_I units (see text)

Decomposition of AHV to V_2O_5

The basic V–O network in V_2O_5 (Fig. 5) is very similar to that in AHV (Fig. 9(b)). Decomposition according to:

$$\underset{\text{AHV}}{(NH_4)_2V_6O_{16}} \rightarrow 3V_2O_5 + 2NH_3 + H_2O \tag{7}$$

involves removal of one of the 16 oxygen atoms per "AHV unit", as water, together with two NH_3 molecules. This must involve-rearrangement of the square pyramids so that edges rather than corners are shared. Neighbouring square-pyramids with shared corners in Fig. 9(b) are in the correct orientation for edge sharing as in Fig. 5.

The various AHV reactants, prepared under different conditions, show differing degrees of order [1], so that the V–O network is obviously not very regular and, as the distribution of NH_4^+ ions can also be considerably asymmetrical, this removal of oxygen will almost certainly not be regular. This is borne out by the uncertainty in the uniformity of the structure of V_2O_5 catalysts, prepared by decomposition methods [28–30], and by the increased crystallinity of the V_2O_5 product of the decomposition in oxidizing atmospheres [1], where the special effect of oxygen exchange with the V_2O_5 lattice has been discussed [3].

Reduction to VO_2

When AHV is decomposed further in ammonia, reduction to VO_2 occurs via the partially reduced intermediate, $(NH_4)_2O \cdot 2VO_2 \cdot 5V_2O_5$, [1], the structure of which is not known.

VO_2 [31] has space group $P2_1/c$ and the structure may be described as consisting of distorted VO_6 octahedra joined by edges to form strings which are, in turn, mutually connected by corners to form a three-dimensional network of a deformed rutile type.

Although the gaseous products have not been analyzed, further removal of oxygen from the V–O network must involve the oxidation of ammonia. This exothermic process occurs on a small scale in the removal of the last traces of NH_3 from the V_2O_5 product formed in non-reducing atmospheres [2, 32].

Conclusion

The course of the decomposition of AMV can be described, from a structural point of view, in terms of relatively small atomic movements. The ready reversibility of the decomposition reaction, the lack of evidence for recrystallization during decomposition, and the formation of a pseudomorph of the reactant crystallite as the decomposition product, suggest that there is a high degree of structural control on the course of the reaction [33–35].

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References

1. M. E. Brown and B. V. Stewart, J. Thermal Anal., 2 (1970) 287.
2. M. E. Brown and B. V. Stewart, Thermal Analysis (Proc. of the 3rd ICTA, Davos, 1971), H. G. Wiedemann Birkhäuser, Basel, 1972, p. 313.
3. M. E. Brown, L. Glasser and B. V. Stewart, J. Thermal Anal., Part II, in press.
4. M. E. Brown, L. Glasser and B. V. Stewart, Progress in Vacuum Microbalance Techniques, Vol. 2 (Heyden and Son, London, 1973), p. 125.
5. J. S. Lukesh, Acta Cryst., 3 (1950) 476.
6. H. E. Swanson, N. T. Gilfrich, M. I. Cook, R. Stinchfield and P. C. Parks, Natl. Bur. Std., Circular, 8 (1959) 539.
7. H. T. Evans, Z. Krist., 114 (1960) 257.
8. V. Synecek and F. Hanic, Physic. J. Czech., 4 (1954) 120.
9. A. D. Kelmers, J. Inorg. Nucl. Chem., 21 (1961) 45.
10. H. T. Evans and S. Block, Inorg. Chem., 5 (1966) 1808.
11. A. Byström, K. A. Wilhelmi and O. Brotzen, Acta Chem. Scand., 4 (1950) 119.
12. H. G. Bachmann, F. R. Ahmed and W. H. Barnes, Z. Krist., 115 (1961) 110.
13. H. G. Bachmann and W. H. Barnes, Z. Krist., 115 (1961) 215.
14. A. Magneli and B. Blomberg, Acta Chem. Scand., 5 (1951) 585.
15. C. Calvo, Ph. D. Thesis, Rutgers University, 1954.
16. M. Lacharte, Bull. Soc. Chim. France, 35 (1924) 321.
17. J. Lamure and G. Colin, Compt. Rend., 258 (1964) 6433.
18. J. D. Bernal and A. L. Mackay, Tschermaks Mineral. Petrog. Mitt., 10 (1965) 331.
19. M. D. Cohen and G. M. J. Schmidt, J. Chem. Soc., (1964) 1996.
20. D. Ginsburg, Israel J. Chem., 10 (1972) 63.
21. A. P. Bolton and R. L. Mays, Chimica Industria, Milan, 52 (1970) 121.
22. A. P. Bolton and M. A. Lanewala, J. Catalysis, 18 (1970) 154.
23. G. T. Kerr, J. Catalysis, 15 (1969) 200.
24. T. H. K. Barron and E. A. Boucher, Reactivity of Solids, Bristol 1972, ed. J. S. Anderson, M. W. Roberts and F. S. Stone, Chapman and Hall, London, 1972, p. 472.
25. E. A. Boucher, D. H. Everett, P. L. Millard and K. R. Sharma, ibid, p. 492.
26. D. H. Everett and E. Redman, Proc. Chem. Soc., (1963) 91.
27. D. H. Davies, D. H. Everett and D. J. Taylor, Trans. Faraday Soc., 67 (1971) 382.
28. S. K. Bhattacharyya and P. Mahanti, J. Catalysis, 20 (1971) 10.
29. I. B. Patrina and V. A. Ioffe, Soviet Phys., Solid State, English Transl., 6 (1964) 2227.
30. G. L. Simard, J. F. Steger, R. J. Arnott and L. A. Siegel, Ind. Eng. Chem., 47 (1955) 1424.
31. G. Andersson, Acta Chem. Scand., 10 (1956) 623.
32. M. Taniguchi and T. R. Ingraham, Can. J. Chem., 42 (1964) 2467.
33. M. D. Cohen, Plenary Lecture, Reactivity of Solids, Bristol 1972, ed. J. S. Anderson, M. W. Roberts and F. S. Stone, Chapman and Hall, London, 1972, p. 456.
34. B. G. Hyde, Plenary Lecture, ibid, p. 23.
35. L. S. Dent Glasser, F. P. Glasser and H. F. W. Taylor, Quart. Rev., London, 16 (1962) 343.

Résumé — On a rapproché les données structurales du métavanadate d'ammonium (MVA) avec celles relatives à la cinétique et à la thermodynamique de la décomposition thermique du MVA, pour étudier le produit intermédiaire important de la décomposition, l'hexavanadate d'ammonium (HVA) et le pentoxyde de vanadium. On discute en détail le produit de la décomposition obtenu en atmosphère non réductrice afin d'obtenir des données sur les mouvements atomiques mis en jeu pendant la décomposition.

La décomposition du MVA s'effectue avec scission des chaines V — O dans la structure du MVA, accompagnée d'un dégagement de gaz ammoniac et d'eau et suivie d'un réarrangement et d'une réticulation d'unités discrètes $V_3O_8^-$, pour former HVA. La décomposition ultérieure en V_2O_5 suit un processus similaire mais moins bien ordonné.

ZUSAMMENFASSUNG — Die Kinetik und thermische Zersetzung von Ammoniummetavanadat (AMV) wurden mit der zu erhaltenden Information über die Strukturen des AMV, des wichtigen Zwischenproduktes der Zersetzung, des Ammoniumhexavanadats (AHV) sowie des Vanadiumpentoxids verbunden. Das in nichtreduzierenden Atmosphären erhaltene Zersetzungsprodukt wurde eingehend erörtert um die in der Zersetzung mit inbegriffenen Atombewegungen zu studieren.

Bei der Zersetzung von AMV spielt eine Spaltung der V—O-Ketten in der Struktur des AMV mit (welche durch eine gleichzeitige Entwicklung von gasförmigen Ammoniak und Wasser begleitet wird), dieser folgt eine Neuordnung und Raumvernetzung diskreter Einheiten auf $V_3O_8^-$-Basis um zur Bildung von AHV zu führen. Die weitere Zersetzung zu V_2O_5 ist ein ähnlicher, obwohl weniger geordneter Vorgang.

Резюме — Кинетические и термодинамические данные о термораспаде метаванадата аммония (АМВ) объединены с информацией о структурах АМВ, интересного промежуточного продукта распада, гексаванадата аммония (АГВ) и пятиокиси ванадия. Подробно обсуждены данные о продукте распада в невосстанавливающих средах и возможности атомых движений, включенных в процесс распада.

При распада АМВ происходит разрыв И—О цепей в его структуре (сопровождаемый одновременным выделением газообразного аммиака и воды) с последующей перегруппировкой и сшивкой отдельных единиц, основанных на $V_3O_8^-$, с образованием АГВ. Дальнейший распад до V_2O_5 является аналогичным, но менее направленным процессом.