The Thermal Decomposition of Ammonium Metavanadate(V) in Open and Closed Systems

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Z. Naturforsch. 43b, 309–317 (1988); received November 9, 1987

Ammonium Metavanadate(V), Thermal Decomposition, High-pressure Reactions, Hydrothermal Reactions

The thermal decomposition of ammonium metavanadate(V) has been studied at atmospheric pressure, at hydrothermal, and high-pressure conditions, respectively. In a closed high-pressure system a redox reaction between vanadium(V) and ammonia takes place, to yield with increasing temperature the compounds \((\text{NH}_4)_2\text{V}_6\text{O}_{12}(\text{OH})_2\), \(\text{VO}_3^(-)(\text{OH})_A\), and \(\text{V}_2\text{O}_5\)\(_A\), the composition of the product eventually approaching \(\text{V}_2\text{O}_5\) at 1100 °C. All these compounds can easily be converted into \(\text{V}_2\text{O}_5\) by heating in air. The mid-infrared spectra of the decomposition products obtained by slow heating of \(\text{NH}_4\text{VO}_3\) in air, are virtually identical and show that ammonium hexavanadate(V), \((\text{NH}_4)_2\text{V}_6\text{O}_{12}\), is the most important, and perhaps only, intermediate in the “non-reduction” case. On further heating, \((\text{NH}_4)_2\text{V}_2\text{O}_5\) may not only loose ammonia and water to form \(\text{V}_2\text{O}_5\) but could as well partially be reduced by ammonia. This could explain the diversity of intermediate “compounds” described in the literature. Hydrothermal reaction of \(\text{NH}_4\text{VO}_3\), yielded \((\text{NH}_4)_2\text{V}_2\text{O}_5\), \((\text{NH}_4)_2\text{V}_3\text{O}_8\), and \(\text{V}_2\text{O}_5\) at rather low temperatures.

Introduction

For the recovery of vanadium from vanadium-bearing titano-magnetite ores, the world’s most important source for vanadium, most technical processes make use of a roast-leach technique which converts the spinel-type vanadium compounds into ammonium metavanadate(V). According to the overall reaction

\[
2\text{NH}_4\text{VO}_3 \rightarrow \text{V}_2\text{O}_5 + 2\text{NH}_3 + \text{H}_2\text{O} \quad (1)
\]

the thermal decomposition of \(\text{NH}_4\text{VO}_3\) eventually yields vanadium pentoxide, \(\text{V}_2\text{O}_5\), which is widely used as catalyst and precursor for other vanadium compounds and metallic vanadium itself [1]. In spite of the very simple form of equation (1), however, the mechanism of the decomposition reaction seems to be much more complicated [2—12], as was discussed elsewhere [13]. Especially the rôle of intermediates with an oxidation number less than five for vanadium is still the subject of controversy.

Most authors agree that ammonium hexavanadate(V), \((\text{NH}_4)_2\text{V}_6\text{O}_{12}\), is the first decomposition product of \(\text{NH}_4\text{VO}_3\) when heated in air in an open system. Other intermediates have been found but not fully characterized up to now. This is mainly due to the fact that many of the decomposition products are very poorly crystalline, sometimes even amorphous. So it cannot be decided by X-ray methods, whether the phases obtained are homogeneous or not. Obviously, chemical analyses are of little value in these cases.

A careful inspection of the literature data shows that nearly all of the previous investigations have been carried out at non-equilibrium conditions, e.g. under a stream of oxidizing, reducing or inert gases or in vacuo. This might well be the reason for the contradictory results. From a chemical point of view, a reaction following equation (1) is rather unexpected, because vanadium(V) is well known for its oxidizing power, whereas ammonium ions can act as a mild reducing agent.

So one would expect under equilibrium conditions a reaction sequence quite different from that observed in non-equilibrium experiments.

The purpose of the present paper is (i) to present new spectroscopic data for the thermal decomposition of \(\text{NH}_4\text{VO}_3\) in open systems,
(ii) to give results for the thermal decomposition of 
NH₄VO₃ in a closed high-pressure system, in 
other words, under equilibrium conditions.

In contrast to the open-system reactions, in the 
latter case a well-defined sequence of reaction prod-
ucts can be found, all with an oxidation number less 
than five for vanadium, eventually approaching va-
nadium(III). All these reaction products can easily 
be converted into V₂O₅ by heating in air.

**Experimental**

Reagent grade NH₄VO₃ (Ventron) has been 
purified by recrystallization [14, 15]. Guinier dia-
grams showed the product to be single phase. The 
refined lattice parameters agreed well with published 
data [16]. The high-pressure experiments were 
performed in a modified Belt-type apparatus using caps-
ules made from silver. Experimental details have 
been described elsewhere [17]. After reaction at the 
desired p, T-conditions (reaction time was usually 
30 min) the samples were quenched to ambient con-
ditions and investigated by X-ray methods (HUBER 
Guinier System 600 for microcrystalline samples; En-
raf-Nonius CAD 4 for single crystals), microscopic 
examination, and chemical analysis. For some hydro-
thermal runs commercial 50 ml autoclaves 
(A. Hofer, Mülheim) were used with the samples 
enclosed in tubes of silver or silica glass.

In the case of the spectroscopic measurements, the 
samples were slowly heated in an oven under atmos-
pheric conditions in open containers between 25 and 
200 °C. The infrared spectra of all these reaction 
products have been recorded on a Bruker 113 V FT-
IR spectrophotometer in the form of nujol-mulls on 
KBr-windows.

**The IR Spectra of Decomposition Products 
of NH₄VO₃**

The temperature and pressure dependence of the 
vibrational spectra of NH₄VO₃ have been discussed 
elsewhere [18]. In the present study the mid-infrared 
spectra of some of the individual decomposition 
products of NH₄VO₃ are reported.

If NH₄VO₃ is slowly heated in an open container 
under non-reducing conditions at temperatures be-
tween 50 and 200 °C, at least three differently col-
oured substances can be identified with the eye, v.i.z. 
an orange-yellow substance, followed by a brown, 
and then finally a black substance. In the literature 
[8—10] these phases have tentatively been identified 
as (NH₄)₂V₂O₇, (NH₄)₂V₄O₁₆, and (NH₄)₂V₃O₂₁, 
resp., according to weight loss considerations, se-
quence of appearance, and colour. Because the sub-
stances obtained are nearly amorphous, a characteri-
zation by means of X-ray methods is impossible. In 
this situation vibrational spectra could perhaps help 
to identify the decomposition products. Unfortu-
nately, very little is known about either the crystal-
lographic or spectroscopic properties of the supposed 
ammonium polyvanadates, except that (NH₄₄)₂V₂O₇₆ 
[19—21] belongs to the same space group P₂₁/m as 
the alkali hexavanadates (A = K, Rb, Cs) [22] 
and that its lattice constants are virtually equal to 
those of the rubidium compound [22]. Octavanada-
dates A₂V₆O₂₁ have been characterized so far only 
for A = K or Rb [23]. The following discussion is 
therefore based on details of the vibrational spectra 
of NH₄VO₃ [18] as well as on the structural and spec-
troscopic properties of alkali metal hexavanadates 
[22] and octavanadates [23].

The mid-infrared spectra of NH₄VO₃ are well-
known [18]; the corresponding spectrum of its 
orange-yellow decomposition product is shown in 
Fig. 1. In NH₄VO₃, chains of corner-shared VO₄-te-
rhedra exist containing V—O terminal and V—O 
bridging bonds. It has been shown [18] that the bands 
at 686/502 cm⁻¹ can be assigned to the V—O bridging 
stretching modes (V—O = 1.803 Å) and the bands at 
891/917 cm⁻¹ to the V—O terminal stretching modes 
(V—O = 1.640—1.647 Å).

The infrared spectrum of the decomposition prod-
uct shown in Fig. 1 is characterized by a limited 
number of NH₄⁺ vibrational bands compared to the 
corresponding ones in NH₄VO₃. Sharp and intense 
V—O bands occur at 1005 and 969 cm⁻¹ respectively. 
The remaining lower frequency components also 
show that significant differences exist between the 
infrared spectra of NH₄VO₃ and its decomposition 
products. In the alkali metal hexavanadates 
A₂V₆O₂₁; A = K, Rb, Cs; the coordination sphere of 
vanadium is characterized by a square-pyramidal 
configuration, with a sixth ligand coordinated 
through the base of the pyramid [22]. In addition to 
the single pyramids, double pyramids or V₆O₉ groups 
are also found in the structure of the hexavanadates. 
One very short bond distance (for example, 1.58 Å 
in K₂V₆O₁₆) and an elongated sixth bond length are 
very characteristic features of the structure [22]. It 
can therefore be expected that V=O vibrational 
bands will be characteristic of the spectra of these 
compounds. Therefore, in accordance with previous
infrared studies of the hexavanadates [24] the bands at 1005 and 969 cm$^{-1}$ in the decomposition products are assigned to V=O stretching modes. Using the parameters of Brown-Shannon [25] V=O bond lengths of 1.596 and 1.620 Å are calculated for (NH$_4$)$_2$V$_6$O$_{16}$, which are nearly identical to those for the rubidium compound. This can be understood if the virtually identical lattice parameters of Rb$_2$V$_6$O$_{16}$ and (NH$_4$)$_2$V$_6$O$_{16}$ are also considered [22]. The intensity ratio of these bands of ca. 1:2 would also be in agreement with the existence of the one V=O group in the single VO$_5$ pyramid and the two appearing in the V$_2$O$_6$ double pyramid. The decomposition products of NH$_4$VO$_3$ show a single N−H stretching mode at 3219 cm$^{-1}$ in addition to a N−H bending mode at 1407 cm$^{-1}$. Comparing the shape of these features with those observed in disordered NH$_4$I [26] and NH$_4$PF$_6$ [27], and keeping in mind the fact that only one of the two stretching modes ($\nu_3(A_1)$ and $\nu_3(F_2)$) is observed, one can assume with a fair amount of certainty that the NH$_4^+$ ions in (NH$_4$)$_2$V$_6$O$_{16}$ have a great deal of reorientational freedom. Without any disorder in these groups one would expect the relative low site symmetry (C$_s$) of the NH$_4^+$-groups in (NH$_4$)$_2$V$_6$O$_{16}$ to cause a splitting of degenerate vibrations like $\nu_3$(N−H stretch) at 3219 cm$^{-1}$ and $\nu_4$(H−N−H bend) at 1407 cm$^{-1}$.

It is, however, rather surprising that the orange-yellow, brown, and black decomposition products (the latter two are not shown in Fig. 1) all give rise to virtually identical mid-infrared spectra. The only difference between the spectra of the orange and black products is in the relative intensities of the NH$_4^+$ and V=O bonds, showing that, in spite of the differences in the colours, these compounds are structurally very similar, or even identical.
It has been reported [23] that Rb$_2$V$_8$O$_{16}$ decomposes at 750–800 °C and 10 kbar according to the equation
\[ 4 \text{Rb}_2\text{V}_8\text{O}_{16} \rightarrow 3 \text{Rb}_2\text{V}_8\text{O}_{21} + \text{Rb}_2\text{O}. \]

In the case of the NH$_4^+$-compound, there is no reason why a similar decomposition should not occur, viz.
\[ 4 \text{(NH}_4\text{)}_2\text{V}_8\text{O}_{16} \rightarrow 3 (\text{NH}_4)_2\text{V}_8\text{O}_{21} + 2 \text{NH}_3 + \text{H}_2\text{O}. \]

Since the latter involves the evolution of NH$_3$ and H$_2$O instead of Rb$_2$O, it could possibly occur at much lower temperatures than for the rubidium compound. The crystals of Rb$_2$V$_8$O$_{21}$ are black and it can be assumed that (NH$_4$)$_2$V$_8$O$_{21}$ will also be of the same colour, if it indeed exists, thus explaining the occurrence of black crystals in the reaction mixture. However, the spectra of the decomposition products are so similar that they fail to explain the structural differences which exist between hexa- and octavanadates [23].

It can therefore be concluded that if NH$_4$VO$_3$ is slowly heated, the decomposition starts at rather low temperatures firstly with the formation of orange-yellow compounds and later with the formation of brown and black compounds. The infrared spectra of these compounds are virtually identical and in agreement with those of the alkali metal hexavanadates in which very characteristic V=O bonds are present in both the single pyramidal VO$_3$ and double pyramidal V$_2$O$_8$ group. In the ammonium hexavanadate, the NH$_4^+$ ion is surrounded by ten anions and appears to have a great deal of reorientational freedom. The temperature dependence of the N–H bands in NH$_4$VO$_3$ showed that although the cations are also surrounded by ten anions, hydrogen bonds to only six anions are formed, and in this six-coordinated structure the two bifurcated hydrogen bonds increase in strength with increasing temperatures, while the strong hydrogen bonds decrease in strength. In other words, the situation is likely to develop that all bonds will be equal in strength and it could be that they will be fluxional [18]. A similar situation is very likely to exist in (NH$_4$)$_2$V$_8$O$_{16}$. No evidence could be found in the mid-infrared spectra of the decomposition products of NH$_4$VO$_3$ for the existence of compounds such as (NH$_4$)$_2$V$_8$O$_{11}$ or (NH$_4$)$_2$V$_8$O$_{21}$ even though the conversion of the ammonium hexavanadate into the latter compound is a very likely prospect.

**High-pressure Reactions of NH$_4$VO$_3$**

Fig. 2 shows the products which are obtained after high-pressure treatment of NH$_4$VO$_3$ at 20–40 kbar, 400–1100 °C, and subsequent quenching to ambient conditions. Depending on the reaction conditions applied, some well-defined regions of decomposition products are found. With the exception of phases labelled A and B in Fig. 2, all these decomposition products were obtained in a rather well-crystallized form, so that complete crystal structure determination could be performed.

NH$_4$VO$_3$ is stable up to 500 °C at 20 kbar, and up to 550 °C at 40 kbar (region a, Fig. 2). At the upper temperature limit of region a a new phase (phase B) has been found which could not yet be identified.

Conditions for the formation of a previously unknown ammonium vanadate(IV) with composition (NH$_4$)$_2$V$_8$O$_{12}$(OH)$_2$ are p = 20–40 kbar, and T = 550–750 °C (region b, Fig. 2). The structure of (NH$_4$)$_2$V$_8$O$_{12}$(OH)$_2$ [28] comprises VO$_6$ octahedra which share corners, edges, and faces to form a new type of a layered structure (Fig. 3). The ammonium ions, situated between the vanadium-oxygen layers, are surrounded by twelve oxygens with distances ranging from 2.9 to 3.4 Å. On heating in nitrogen at 1 bar, (NH$_4$)$_2$V$_8$O$_{12}$(OH)$_2$ decomposes at 390 °C according to the equation

\[ (\text{NH}_4)_2\text{V}_8\text{O}_{12}$(OH)$_2$ \rightarrow 6 \text{VO}_2 + 2 \text{NH}_3 + 2 \text{H}_2\text{O}. \]

Heating in air eventually yields vanadium pentoxide, V$_2$O$_5$.

At still higher temperatures (region c, Fig. 2) ammonia is completely lost, and mixed-valence vanadium oxide hydroxides VO$_2$–x(OH)$_x$ are formed which already have been described elsewhere [29]. The actual composition depends on the reaction conditions with a tendency for increasing δ with increasing temperatures (Fig. 4, from [29]). In the present investigation, phases with 0.1 < δ < 0.4 were obtained. These compounds, which can also be obtained by reduction of VO$_2$ with hydrogen [30], crystallize with the CaCl$_2$-type structure, a distorted variant of the rutile-type structure.

Following Bärnighausen et al. [31, 32], the geometrical features of the CaCl$_2$-type structure can be described by two angles $\omega$ and $\omega'$, defined by the equations

\[ \tan \left( \frac{\pi}{4} + \omega \right) = \frac{a(1/2 - x)}{b(1/2 - y)}, \]
Fig. 2. Decomposition products of NH₄VO₃ recovered after high-pressure reaction at the p, T-conditions indicated.

Fig. 3. Part of the crystal structure of (NH₄)₂V₆O₁₂(OH)₂, showing the vanadium-oxygen layers.
and
\[ \tan(\pi/4 - \omega') = a \cdot x \sqrt{b \cdot y}. \]

\( \omega \) is the tilt-angle of the cation coordination octahedra with respect to the rutile-type structure. A parameter \( f = \omega' / \omega \) characterizes small distortions of the cation coordination octahedron as the result of interactions between the anions. From the lattice parameters and atomic positions of \( \text{V}_2\text{O}_{1.75}\text{(OH)}_{0.25} \) [29] the values \( \omega = 2.96^\circ, \omega' = 3.23^\circ, \) and \( f = 1.09 \) can be calculated. According to Bärnighausen et al. [31, 32] the latter is a definite sign for the presence of hydrogen bonds in the anion lattice.

At the highest temperatures investigated (region \( d \), Fig. 2) even hydroxyl groups are no longer present in the reaction products, and a series of Magnéli-type vanadium oxides \( \text{V}_n\text{O}_{2n-1} (2 \leq n \leq 6) \) is formed which can be synthesized conveniently in this way.

From Fig. 2 the systematic evolution of the sequence of phases with decreasing \( n \) for increasing temperatures can be visualized. This sequence terminates at \( n = 2 \) (e.g. \( \text{V}_2\text{O}_3 \)) showing that under the conditions applied no further reduction of vanadium is possible. Additional runs not shown in Fig. 2 proved that to be true also for the reaction at 20 kbar, 1500 °C.

**Hydrothermal Reactions of NH\(_4\)VO\(_3\)**

In addition to the "dry" high-pressure reactions ("dry" means that no water other than that coming from the decomposition of \( \text{NH}_4\text{VO}_3 \) was present) some hydrothermal runs at pressures between 100 and 500 bar and temperatures between 300 and 500 °C were performed. Surprisingly enough, under hydrothermal conditions, e.g. with an excess of water, complete transformation of \( \text{NH}_4\text{VO}_3 \) into \( \text{V}_2\text{O}_3 \) has been observed after reaction at 300 bar, 500 °C, for 3 days. At 500 bar, 360 °C, an ammonium vanadium bronze of approximate composition \( (\text{NH}_4)_{0.5}\text{V}_2\text{O}_5 \) is formed, similar to that described by Vidonne et al. [33].

If the silver tube is incompletely filled with water, e.g. in the presence of some air, black platelets of \( (\text{NH}_4)_2\text{V}_2\text{O}_8 \) were obtained after keep-

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**Table I. Crystallographic data for \( (\text{NH}_4)_2\text{(VO)}[\text{V}_2\text{O}_5] \).**

<table>
<thead>
<tr>
<th>Space Group</th>
<th>P4bm (No. 100)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Structure type</td>
<td>Fresnoite (Ba(_2)(TiO(_3))[Si(_2)O(_7)])</td>
</tr>
<tr>
<td>Unit cell dimensions</td>
<td>( a = 8.885(2) ) Å, ( c = 5.564(5) ) Å, ( Z = 2 )</td>
</tr>
<tr>
<td>Diffractometer</td>
<td>CAD 4 (Enraf Nonius)</td>
</tr>
<tr>
<td>Reflections measured</td>
<td>2069 (0 ( \leq h \leq 17 ), 0 ( \leq k \leq 17 ), 0 ( \leq l \leq 11 ))</td>
</tr>
<tr>
<td>Unique reflections</td>
<td>550 with ( I &gt; 3\sigma(I) )</td>
</tr>
<tr>
<td>Final Residuals</td>
<td>( R = 0.029, R_w = 0.032 )</td>
</tr>
</tbody>
</table>

| Positional parameters and equivalent isotropic temperature factors: |
|-----------------|-----------|-----------------|---------------|
| Atom Position   | \( x \)   | \( y \)   | \( z \)   | \( B_{eq}[\text{Å}^2] \) |
| N               | 4c        | 0.3301(3)     | 0.8301(3)     | 0.9623(7)     | 2.42 |
| V(1)            | 2a        | 0             | 0             | 0.4940(2)     | 0.98 |
| V(2)            | 4c        | 0.1335(1)     | 0.6335(1)     | 0.49*         | 0.89 |
| O(1)            | 8d        | 0.0853(2)     | 0.8070(2)     | 0.6037(5)     | 1.74 |
| O(2)            | 4c        | 0.1304(2)     | 0.6304(2)     | 0.1993(6)     | 1.83 |
| O(3)            | 2b        | 0             | 0.5           | 0.6088(7)     | 1.53 |
| O(4)            | 2a        | 0             | 0             | 0.2108(8)     | 2.94 |

* For an easy comparison with \( \text{K}_2\text{V}_3\text{O}_8 \) [35], the \( z \)-parameter of \( V(2) \) was fixed to define the origin.
ing $\text{NH}_4\text{VO}_3$ at 500 bar and 380 °C for 5 days. The results of a single-crystal X-ray structure analysis [13] are presented in Table I. They agree rather well with the data given by Theobald et al. [34] and show that the compound in fact is an ammonium oxovanadium(IV)divanadate(V) and should be formulated as $(\text{NH}_4)_2(\text{VO})(\text{V}_2\text{O}_7)$.

**Conclusions**

The results of the present investigation are summarized in Fig. 5. It shows the reaction pathways for the thermal decomposition of $\text{NH}_4\text{VO}_3$ under different conditions. Only those reaction products which have been fully characterized by their Guinier pattern and/or complete crystal structure analyses have been included in Fig. 5. It has been demonstrated for the first time that the expected redox reaction between vanadium(V) and $\text{NH}_3$ indeed takes place at high pressures, e.g. under closed system conditions. It should be emphasized, however, that the phases obtained are almost certainly no true high pressure phases, the effect of pressure being merely to keep the reactants together and to prevent losses of ammonia and water during the high temperature reactions. Neglecting the yet unidentified phase B, which appears only in a very small $p$, $T$-region (cf. Fig. 2), the essential steps for the thermal decomposition of $\text{NH}_4\text{VO}_3$ in closed system are the following:

i) $6 \text{NH}_4\text{VO}_3 \xrightarrow{550-650 \degree C} (\text{NH}_4)_2\text{V}_6\text{O}_{12}(\text{OH})_2 + 4 \text{H}_2\text{O} + 2 \text{NH}_3 + \text{N}_2$
   (region b, Fig. 2),

ii) $\text{NH}_4\text{VO}_3 \xrightarrow{700-800 \degree C} \text{VO}_2\delta(\text{OH})_\delta + \text{H}_2\text{O} + \left(\frac{2-\delta}{3}\right) \text{NH}_3 + \left(\frac{1+\delta}{6}\right) \text{N}_2$
   (region c, Fig. 2),

iii) $n \text{NH}_4\text{VO}_3 \xrightarrow{800-1100 \degree C} \text{V}_{n}\text{O}_{2n-1} + (n+1)\text{H}_2\text{O} + \left(\frac{2n-2}{3}\right) \text{NH}_3 + \left(\frac{n+2}{6}\right) \text{N}_2$
   (region d, Fig. 2).

![Fig. 5. Reaction pathways for the thermal decomposition of $\text{NH}_4\text{VO}_3$ at different conditions.](image-url)
Further reactions of the phases obtained according to (i) and (ii) are possible, but are of course dependent on the reaction conditions. In all cases, however, V$_2$O$_5$ is the final product provided that the ammonia necessary for reduction is kept in the system. For instance, (NH$_4$)$_2$V$_6$O$_{12}$(OH)$_2$ can react according to the equations

\[(\text{NH}_4)_2\text{V}_6\text{O}_{12}(\text{OH})_2 \xrightarrow{20 \text{kbar} > 1000 ^\circ\text{C}} 3\text{V}_2\text{O}_3 + 5\text{H}_2\text{O} + \text{N}_2,\]

\[(\text{NH}_4)_2\text{V}_6\text{O}_{12}(\text{OH})_2 \xrightarrow{1\text{bar}, \text{N}_2 \text{ at } 400 ^\circ\text{C}} 6\text{VO}_2 + 2\text{NH}_3 + 2\text{H}_2\text{O},\]

or

\[(\text{NH}_4)_2\text{V}_6\text{O}_{12}(\text{OH})_2 + \frac{3}{2} \text{O}_2 \xrightarrow{1\text{bar, air at } 500 ^\circ\text{C}} 3\text{V}_2\text{O}_5 + 2\text{NH}_3 + 2\text{H}_2\text{O},\]

depending on whether the heating is performed in a closed high-pressure system, at 1 bar in an inert gas atmosphere, or at 1 bar in air, respectively.

Compared to the high-pressure reactions the thermal decomposition of NH$_4$VO$_3$ at atmospheric pressure seems to be much more complicated. We believe that the main reason for this behaviour is the fact that for the two limiting cases of reaction pathways, e.g. complete reduction (V(V) → V(III)) and complete non-reduction (V(V) → V(V)) it is much more difficult to approach the latter one. The spectroscopic, X-ray, and analytical evidence points to the formation of ammonium hexavanadate(V), (NH$_4$)$_2$V$_6$O$_{16}$, as the most important, and perhaps only, intermediate in the "non-reduction" case. The colour of the decomposition product can also not be used as a criterion to distinguish between structural types and composition of ammonium vanadates since it was shown that even black and orange-yellow decomposition products of NH$_4$VO$_3$ in the "non-reduction case" give rise to almost identical infrared spectra. In the course of further heating, (NH$_4$)$_2$V$_6$O$_{16}$ may not only loose ammonia and water to form V$_2$O$_5$ but could as well partially be reduced by ammonia. This would explain the diversity of "compounds" described in the literature, which in fact are merely mixtures of reduced and unreduced phases in many cases. The observation that under high-pressure conditions (NH$_4$)$_2$V$_6$O$_{16}$ is quantitatively reduced to VO$_2$ [36] strongly supports this view.

In the presence of excess water, e.g. under hydrothermal conditions, quite different reactions were found. A general trend towards lower reaction temperatures can be observed. Further work to clarify the situation is on progress.

The financial support given by the Deutsche Forschungsgemeinschaft, the Fonds der Chemischen Industrie, the Alexander von Humboldt-Stiftung, and the University of Pretoria is gratefully acknowledged.
[36] K.-J. Range and Ch. Eglmeier, to be published.