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THE THERMAL DECOMPOSITION OF $(NH_4)[VO(O_2)_2(NH_3)]$

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The compound, $(NH_4)[VO(O_2)_2(NH_3)]$, thermally decomposes to ammonium metavanadate, which then decomposes to vanadium pentoxide. Using a heating rate of 5 $deg \cdot min^{-1}$, the first decomposition step occurs between 74° and 102°C. The transformation degree dependence of the activation energy (α–E) is shown to follow a decreasing convex form, indicating that the first decomposition step is a complex reaction with a change in the limiting stage of the reaction. Infrared spectra indicated that the decomposition proceeds via the gradual reduction of the ratio of the '$(NH_4)_2O$' to 'V_2O_5'units from the original 1:1 ratio in ammonium metavanadate, which may be written as $(NH_4)_2O \cdot V_2O_5$, to V_2O_5.

Keywords: kinetic investigations, $(NH_4)[VO(O_2)_2(NH_3)]$

Introduction

The thermal decomposition of $(NH_4)[VO(O_2)_2(NH_3)]$ was not investigated previously, but should proceed via the formation of ammonium metavanadate. It was shown that the decomposition of NH_4VO_3 does not occur in a single step, but in several steps with intermediates that are very dependent on the conditions of temperature and surrounding atmosphere during decomposition [1, 2].

According to one theory ammonium metavanadate (AMV) decomposes directly or indirectly (depending on ambient conditions) to ammonium hexavanadate, which then decomposes in non-reducing atmospheres to V_2O_5 [1, 3].

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

$$(NH_4)_2V_6O_{16}\ (s) \rightarrow 3V_2O_5\ (s) + 2NH_3\ (g) + H_2O\ (g)$$

These reactions are all endothermic and reversible [1, 2, 4, 5].

Another investigation showed that the stoichiometry of the thermal decomposition of ammonium metavanadate corresponds well to the gradual reduction of the ratio of the '$(NH_4)_2O$' to 'V_2O_5' units from the original 1:1 ratio in ammo-

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nium metavanadate, which may be written as $(NH_4)_2O{\cdot}V_2O_5$, to pure V_2O_5, with ammonia and water being evolved throughout the decomposition product in the mole ratio of 2:1 [1]. The first decomposition product corresponds stoichiometrically to the divanadate form and the second to the hexavanadate (or tri-vanadate) form:

$$\underset{\text{AMV}}{2(NH_4)_2O{\cdot}V_2O_5\ (s)} \rightarrow \underset{\substack{\text{Divanadate}\\ (NH_4)_2V_2O_{11}}}{(NH_4)_2O{\cdot}2V_2O_5\ (s)} + 2NH_3\ (g) + H_2O\ (g)$$

$$\underset{\text{ADV}}{3(NH_4)_2O{\cdot}2V_2O_5\ (s)} \rightarrow \underset{\substack{\text{Hexavanadate}\\ (NH_4)_2V_6O_{16}}}{2(NH_4)_2O{\cdot}3V_2O_5\ (s)} + 2NH_3\ (g) + H_2O\ (g)$$

Some authors could find no evidence for the formation of the divanadate [2]. As a last intermediate the monohydrate of V_2O_5 forms and on further heating V_2O_5 is obtained [6, 7].

In the present investigation an attempt was made to identify the sequence of formation of the decomposition products of $(NH_4)[VO(O_2)_2(NH_3)]$ under a moist nitrogen atmosphere, and to investigate the decomposition kinetics of the first decomposition step.

Before beginning the kinetic analysis of any process, it is essential to make sure whether it is a single or a complex process. Nearly all the analysis methods described in literature were developed for a single stage process [8]. Due to the complexity of the mathematics when complex processes are involved the usual methods of fitting decomposition data to a number of mechanism related equations cannot be used.

As a criterion of a single process, the method described by Vyanzovkin and Lesnikovich was used [9]. Activation energy values at different conversion values are determined from dynamic thermogravimetric data using different heating rates. The transformation-degree dependence of the activation energy is determined by this isoconversion method.

The isoconversion method represents the results of several non-isothermal runs as

$$\ln\left[\frac{d\alpha}{dt}\beta\right] = \ln AF(\alpha) - \left(\frac{E}{RT}\right)$$

where β is the heating rate and T the temperature at the degree of decomposition, α [10, 11]. This can be used to determine the activation energy, E, without identification of the reaction model or $F(\alpha)$, by plotting ln β against $1/T$ at constant α and determine E from the slope of the line.

The existence of a dependence indicates that the process is complex. If activation energy does not change with transformation-degree, decomposition occurs in a single step. A concave decreasing transformation-degree dependence of the activation energy indicates that the process proceeds through an intermediate reversible stage. If the α–E dependence has a decreasing convex form, the process occurs with a change in the limiting stage of the reaction. An increasing α–E dependence indicates that parallel reactions are involved in the decomposition step [9].

Experimental

Sample preparation

Approximately 2 g of ammonium metavanadate was dissolved in 30 ml concentrated hydrogen peroxide. The *pH* was then adjusted to be between 9 and 12 with NH_4OH(aq). The product is obtained by precipitation which occurs upon addition of ethanol. The product is washed with ether and dried in vacuum at room temperature for 6 hours.

Thermogravimetric analysis

A Stanton Redcroft STA 780 simultaneous thermal analyser was used to collect thermogravimetric data. Moist nitrogen was used as a dynamic atmosphere. Alumina sample pans were used and temperature calibration of the equipment was achieved using ICTA recommended DTA standards.

Infra-red spectroscopic analysis

Infra-red spectra were recorded on a Brucker IFS 113V spectrometer between 400 and 4000 cm^{-1}. Samples were prepared in the form of KBr discs.

Results and discussion

The mass-loss curve of $(NH_4)[VO(O_2)_2(NH_3)]$ using a heating rate of 5 deg·min^{-1} is given in Fig. 1. From the curve it seems that at least 3 intermediate compounds from before the endproduct. The infrared spectra of compounds A to D are given in Fig. 2.

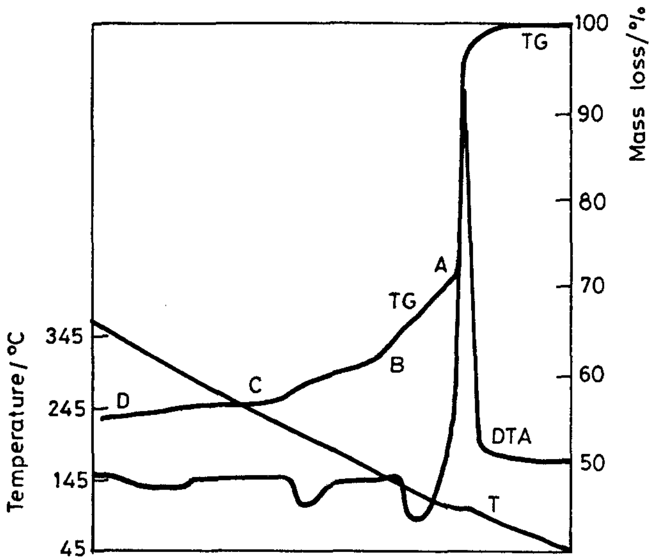

Fig. 1 Mass-loss curve of $(NH_4)[VO(O_2)_2(NH_3)]$ using a heating rate of 5 deg min^{-1} in a moist nitrogen atmosphere

A detailed vibrational analysis of the compound, $(NH_4)[VO(O_2)_2(NH_3)]$, and a discussion of its vibrational spectrum will be reported at a later stage.

Infrared absorption bands of compounds A, B and C are compared to that of NH_4VO_3 and $(NH_4)_2V_6O_{16}$ in Table 1. The IR spectrum of compound A corresponds very well to that of a standard NH_4VO_3 spectrum. The percentage mass loss observed for this decomposition step is 29%, which is close to the theoretical value of 29.5%. Using a heating rate of 5 deg·min^{-1}, this decomposition step occurs between 74° and 102°C. As expected for the loss of peroxide groups, this decomposition step is exothermic as can be seen on the DTA curve (Fig. 1).

The IR spectrum of product B still shows some similarities to that of ammonium metavanadate in the absorbance regions for ammonium, especially in the N–H stretching region between 2700 and 3200 cm^{-1}. The three broad absorption bands are of lower intensity than in product A, as expected during the progress of the decomposition reaction. The two lower wavenumber bands have lower intensities than the band at 3169 cm^{-1} in compound A. This could be an indication of the formation of ammonium hexavanadate, as it shows a N–H stretching mode at 3219 cm^{-1}. The N–H bending mode is splitted into two bands at 1399 and 1440 cm^{-1}, which indicates that a low disorder exists in the relative low site symmetry (C_s) of the NH_4^+ groups in the compound in contrast to that in ammonium hexavanadate which has a great deal of reorientational freedom [2]. The

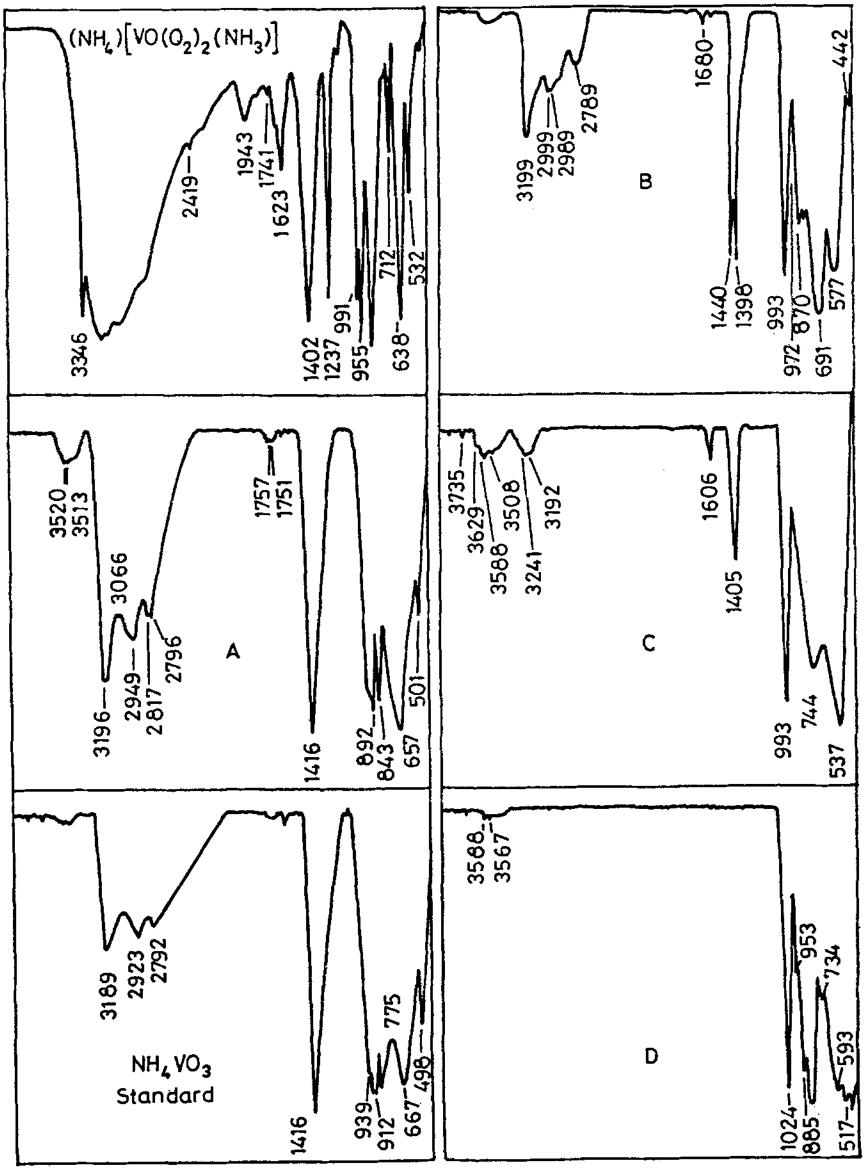

Fig. 2 Infrared spectra of the decomposition products of $(NH_4)[VO(O_2)_2(NH_3)]$

observed V–O vibrations are the same as that for $(NH_4)_2V_6O_{16}$. Only one bands occurs at 993 cm^{-1} instead of the observed for ammonium hexavanadate at 1005 and 969 cm^{-1} [2]. Two additional bands at 870 and 858 cm^{-1} cannot be attributed to $(NH_4)_2V_6O_{16}$, and the band at 581 cm^{-1} in product B is expected around 547 cm^{-1} for $(NH_4)_2V_6O_{16}$. The infrared spectrum of product B shows some resemblance to the spectra of ammonium metavanadate and ammonium hexavanadate, and it thus seems that it could be represented by the formula $(NH_4)_2O{\cdot}3V_2O_5$, which stoichiometrically agrees with ammonium hexavanadate, but with more or less the ammonium metavanadate structure.

Table 1 Infrared absorption bands of products A, B and C compared to NH_4VO_3 and $(NH_4)_2V_6O_{16}$ between 400 and 4000 cm^{-1}

NH_4VO_3	A	B	C	$(NH_4)_2V_6O_{16}$ [2]	Assignment
–	3520	3509	3588	–	Water mode
3189	3196	3196	3192	3219	N–H stretching modes
–	–	3007	–	–	
2923	2949	–	–	–	
2792	2796	2796	–	–	
–	–	1600	1606	–	Water mode
1416	1416	1440	–	–	N–H bending modes
–	–	1399	1405	1407	
–	–	–	–	1005	V–O modes
912	892	993	993	969	
–	–	870	–	–	
–	–	858	–	–	
667	657	692	744	736	
498	501	581	537	547	

The mass loss percentage of the second decomposition step (as determined from the initial compound) is 38.5%, which corresponds to the mass loss of the initial compound through ammonium metavanadate to the stoichiometric ammonium hexavanadate for which the theoretical percentage should be 40.0%. This endothermic reaction took place between 102° and 130°C when a heating rate of 5 deg·min^{-1} is used.

The infrared spectrum of compound C showed some similarities to that of ammonium hexavanadate and vanadium pentoxide, as is shown in Fig. 2 and Table 1. A mass loss of 43% is observed and although it proved difficult to obtain this product an attempt was made to identify it. It seems to have the approximate formula of $(NH_4)_2O{\cdot}7V_2O_5$, which can also be written as $2(NH_3){\cdot}(H_2O){\cdot}{\cdot}7V_2O_5$ [12]. Further investigations to identify this product will be undertaken.

The IR spectra confirmed that the final product, D, is V_2O_5. The observed mass loss (as calculated from the initial compound) is 45% and is the same as the theoretical value. The endothermic decomposition to vanadium pentoxide was completed at 312°C.

Kinetic investigation

Due to the fact that the reaction proceeds very fast at heating rates of 4 deg·min^{-1} and more, various runs were obtained only at heating rates of 0.1 deg·min^{-1} to 3 deg·min^{-1}. Using these heating rates the first decomposition reaction was only completed in 10 minutes to 24 hours and a mass loss of 71% was observed for each of these runs. The data from these runs were used to determine the activation energy values at each fraction reaction value of 0.1 to 0.9, with 0.1 increments. The relationship between E and α is shown in Fig. 3. A convex decreasing E –α relationship is obtained.

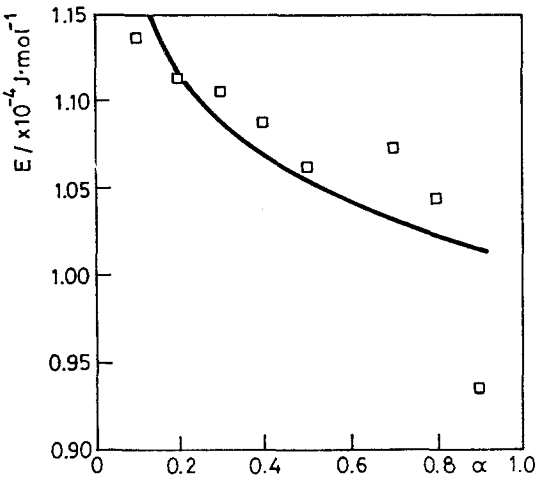

Fig. 3 The transformation-degree dependence of the activation energy for the first decomposition reaction

Conclusion

Results indicate that the decomposition of $(NH_4)[VO(O_2)_2(NH_3)]$ in a moist nitrogen atmosphere can be presented by the following reaction scheme:

$$(NH_4)[VO(O_2)_2(NH_3)]\ (s) \rightarrow NH_4VO_3\ (s) + \text{gases}$$

where NH_4VO_3 can also be written as $(NH_4)_2O{\cdot}V_2O_5$.

Further investigations of the decomposition products of ammonium metavanadate obtained in the previous decomposition reaction will be undertaken. Infrared spectroscopic results indicated that the decomposition of the ammonium metavanadate under moist nitrogen atmosphere seems to follow the following route:

$$(NH_4)_2O{\cdot}V_2O_5\ (s) \rightarrow (NH_4)_2O{\cdot}3V_2O_5\ (s) + \text{gases}$$

where the product has the same stoichiometric composition as ammonium hexavanadate, $(NH_4)_2V_6O_{16}$, but not the same structure;

$$(NH_4)_2O{\cdot}3V_2O_5\ (s) \rightarrow (NH_4)_2O{\cdot}xV_2O_5\ (s) + \text{gases}$$

with x gradually increasing from 3 to approximately 7 and where the product could possibly be written as $2(NH_3)(H_2O){\cdot}7V_2O_5$;

$$(NH_4)_2O{\cdot}7V_2O_5\ (s) \rightarrow V_2O_5\ (s) + \text{gases.}$$

From the convex decreasing $E - \alpha$ relationship it is concluded that the first decomposition step,

$$(NH_4)[VO(O_2)_2(NH_3)]\ (s) \rightarrow NH_4VO_3\ (s) + \text{gases}$$

is not a single process but occurs with a change in the limiting stage of the reaction.

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Zusammenfassung — Die Verbindung $(NH_4)[VO(O_2)_2(NH_3)]$ wird thermisch zuerst zu Ammoniummetavanadat und im Anschluß zu Vanadiumpentoxid zersetzt. Bei einer Aufheizgeschwindigkeit von 5 grad·min^{-1} setzt der erste Zersetzungsschritt zwischen 74° und 102°C ein. Die Abhängigkeit der Aktivierungsenergie von der Konversionsrate (α-E) zeigt als Funktion einen abnehmenden konvexen Verlauf, was zeigt, daß der erste Zersetzungsschritt eine komplexe Reaktion ist. IR-Spektren zeigen, daß die Zersetzung über eine allmähliche Abnahme des Verhältnisses "$(NH_4)_2O$"/V_2O_5 verläuft, beginnend bei einem anfänglichen Verhältnis von 1:1 in Ammoniummetavanadat, was auch als $(NH_4)_2OV_2O_5$ geschrieben werden kann, bis hin zu V_2O_5.