

## THE THERMAL DECOMPOSITION OF $(\text{NH}_4)_4\text{V}_2\text{O}_{11}$ IN A NITROGEN ATMOSPHERE AND THE KINETICS OF THE FIRST DECOMPOSITION STEP

*C. A. Strydom*

DEPARTMENT OF CHEMISTRY, UNIVERSITY OF PRETORIA, PRETORIA, 0002 SOUTH AFRICA

Although the reaction products are unstable at the reaction temperatures, at a heating rate of  $2 \text{ deg}\cdot\text{min}^{-1}$  ammonium peroxy vanadate,  $(\text{NH}_4)_4\text{V}_2\text{O}_{11}$ , decomposes to  $(\text{NH}_4)[\text{VO}(\text{O}_2)_2(\text{NH}_3)]$  (above  $93^\circ\text{C}$ ); this in turn decomposes to  $(\text{NH}_4)[\text{VO}_3(\text{NH}_3)]$  (above  $106^\circ\text{C}$ ) and then to ammonium metavanadate (above  $145^\circ\text{C}$ ). On further heating vanadium pentoxide is formed above  $320^\circ\text{C}$ . The first decomposition reaction occurs in a single step and the Avrami-Erofeev equation with  $n=2$  fits the decomposition data best. An activation energy of  $148.8 \text{ kJ}\cdot\text{mol}^{-1}$  and a  $\ln(A)$  value of 42.2 are calculated for this reaction by the isothermal analysis method. An average value of  $144 \text{ kJ}\cdot\text{mol}^{-1}$  is calculated for the first decomposition reaction using the dynamic heating data and the transformation-degree dependence of temperature at different heating rates.

**Keywords:** ammonium peroxy vanadate, kinetics

### Introduction

In a previous study it was shown that the thermal decomposition of  $(\text{NH}_4)[\text{VO}(\text{O}_2)_2(\text{NH}_3)]$  proceeds via formation of ammonium metavanadate [1]. The related compound  $(\text{NH}_4)_4\text{V}_2\text{O}_{11}$  was prepared and its decomposition might also be expected to proceed via ammonium metavanadate. It was the purpose of this study to identify the decomposition products of  $(\text{NH}_4)_4\text{V}_2\text{O}_{11}$  and to determine the kinetic parameters of the first decomposition step.

Before undertaking a kinetic analysis of any process, it is essential to verify that the process occurs in a single step. Nearly all the analysis methods described in the literature have been developed for a single-stage process [2]. 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 for a single process, the method described by Vyazovkin and Lesnikovich was used [3]. 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

$$\ln [d\alpha / dt \beta] = \ln Af(\alpha) - (E / RT)$$

where  $\beta$  is the heating rate and  $T$  the temperature at the degree of decomposition,  $\alpha$  [4, 5]. This can be used to determine the activation energy,  $E$ , without identification of the reaction model or  $f(\alpha)$ , by plotting  $\ln \beta$  against  $1/T$  at constant  $\alpha$ . Activation energy values are then calculated from the slopes of the curves. The existence of any dependence indicates that the process is complex. If activation energy does not change with transformation-degree, decomposition occurs in a single step.

## Experimental

### *Sample preparation*

Approximately 2g of ammonium metavanadate was dissolved in 30 cm<sup>3</sup> concentrated hydrogen peroxide. The *pH* was then adjusted to between 9 and 12 with NH<sub>4</sub>OH (conc.). A solid compound (NH<sub>4</sub> [VO (O<sub>2</sub>)<sub>2</sub> (NH<sub>3</sub>)]]) was then precipitated on addition of ethanol. This compound was washed with ether and dried under vacuum at room temperature. Approximately 1g of this compound was added to a mixture of 50 cm<sup>3</sup> water with approximately 8 cm<sup>3</sup> hydrogen peroxide. This was stirred until all solids were dissolved and (NH<sub>4</sub>)<sub>4</sub>V<sub>2</sub>O<sub>11</sub> then precipitated on addition of ethanol. The precipitate was washed with ethanol and dried under vacuum at room temperature. The product was identified by infra-red (IR) spectroscopy and X-ray powder diffraction.

### *Thermogravimetric analysis*

A Stanton Redcroft STA 780 simultaneous thermal analyser was used to collect thermogravimetric data. Nitrogen was used as a dynamic atmosphere (flow rate approx. 20 cm<sup>3</sup>·min<sup>-1</sup>). Platinum sample pans were used and temperature calibration was achieved using the ICTA recommended DTA standards. Sample masses varied between 5.0 and 15.0 mg.

### *Infra-red spectroscopic analysis*

IR spectra were recorded on a Brucker IFS 113V spectrometer between 400 and 4000 cm<sup>-1</sup>. Samples were prepared in the form of KBr discs.

## Results and discussion

The mass-loss curve of  $(\text{NH}_4)_4\text{V}_2\text{O}_{11}$  using a heating rate of  $2 \text{ deg}\cdot\text{min}^{-1}$  is given in Fig. 1. From the figure it appears that intermediate products form at mass losses of approximately 5% ( $93^\circ\text{C}$ ), 24% ( $106^\circ\text{C}$ ), 33% ( $145^\circ\text{C}$ ) and 48% ( $320^\circ\text{C}$ ). Reaction temperature ranges do overlap, since no stable intermediates could be obtained even at heating rates as slow as  $0.1 \text{ deg}\cdot\text{min}^{-1}$ . From the DTA curve it is clear that the first two reactions and a reaction towards the end of decomposition are exothermic reactions, while all other reactions are endothermic. The exothermic reaction at approx.  $300^\circ\text{C}$  seems to be a phase transition of  $\text{V}_2\text{O}_5$ , which will be discussed in a later paper.

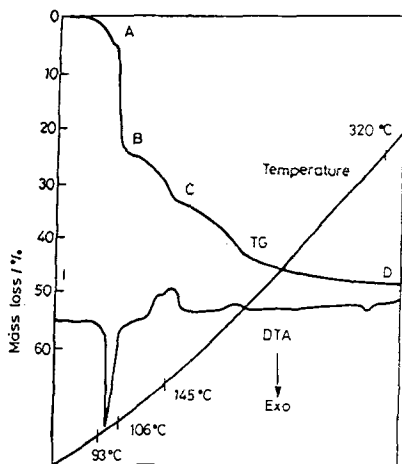


Fig. 1 Mass-loss and DTA curve of the thermal decomposition of  $(\text{NH}_4)_4\text{V}_2\text{O}_{11}$  using a heating rate of  $2 \text{ deg}\cdot\text{min}^{-1}$

An attempt was made to obtain IR spectra of each of the intermediate products by stopping the reactions and cooling to room temperature immediately as the appropriate mass loss was reached. IR spectra of the decomposition products (5% A, 24% B, 33% C, and 48% D) are given in Fig. 2, as well as spectra of ammonium metavanadate, vanadium pentoxide,  $(\text{NH}_4)_4\text{V}_2\text{O}_{11}$ , and  $\text{NH}_4[\text{VO}(\text{O}_2)_2(\text{NH}_3)]$ . From this figure it is clear that the intermediate product (A) formed at a mass-loss of 5% is  $\text{NH}_4[\text{VO}(\text{O}_2)_2(\text{NH}_3)]$ , the product (C) formed at a mass-loss of 33% is ammonium metavanadate, and the product (D) formed at a mass-loss of 48% is vanadium pentoxide. The intermediate product (B) formed at a mass-loss of 24% has all the IR peaks of ammonium metavanadate, but with stronger N-H bending ( $1617 \text{ cm}^{-1}$ ) and stretching ( $3201$  and  $2957 \text{ cm}^{-1}$ ) modes. These modes are also the main  $\text{NH}_3$  modes that appear in ammonia complexes [6]. Product (B) thus seems

to be  $\text{NH}_4[\text{VO}_3(\text{NH}_3)]$ , which could result from loss of a peroxide group from  $\text{NH}_4[\text{VO}(\text{O}_2)_2(\text{NH}_3)]$ . Observed and calculated mass losses for the A to D reaction products compare well (Table 1).

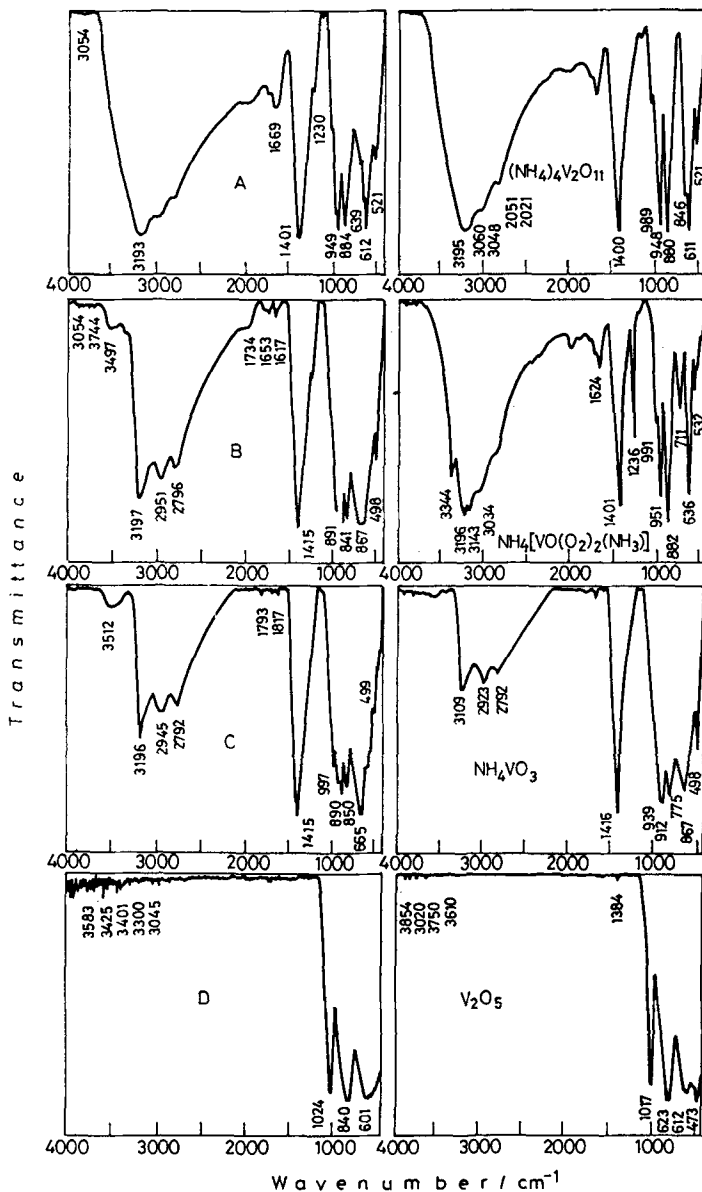


Fig. 2 IR spectra of the decomposition products of  $(\text{NH}_4)_4\text{V}_2\text{O}_{11}$

**Table 1** Observed and calculated mass losses for the decomposition products of ammonium peroxovanadate

Reaction product	Observed mass loss*/	Calculated mass loss*/
	%	%
NH <sub>4</sub> [VO(O <sub>2</sub> ) <sub>2</sub> (NH <sub>3</sub> )]	5	5.2
NH <sub>4</sub> [VO <sub>3</sub> (NH <sub>3</sub> )]	24	23.4
NH <sub>4</sub> VO <sub>3</sub>	33	33.2
V <sub>2</sub> O <sub>5</sub>	48	48.1

\*All mass loss percentages calculated from (NH<sub>4</sub>)<sub>4</sub>V<sub>2</sub>O<sub>11</sub>

The activation energy values at transformation degree values ( $\alpha$ ) of 0.1 to 0.9 were determined from the slopes of the curves of  $\ln \beta$  against reciprocal temperature, as described in the introduction. Since the reaction proceeds too fast at higher heating rates, data were collected at heating rates of 4.0 deg·min<sup>-1</sup> and lower, the lowest heating rate being 0.1 deg·min<sup>-1</sup>. The activation energy ( $E$ ) dependence of  $\alpha$  is given in Table 2. From this table it is clear that up to an  $\alpha$  value of 0.7,  $E$  is not dependent on the transformation degree ( $\alpha$ ). Figure 1 indicates that the decomposition reactions overlap, and it can be concluded that at an  $\alpha$  value of 0.7 the next reaction is starting. From this table an activation energy value of 144 kJ·mol<sup>-1</sup> is estimated for the first decomposition reaction, i.e. the removal of a water molecule from the ammonium peroxovanadium compound.

**Table 2** Activation energy values ( $E$ ) at different transformation-degree values ( $\alpha$ )

Transformation-degree /	Activation-energy ( $E$ ) /
$\alpha$	kJ·mol <sup>-1</sup>
0.1	142.9
0.2	144.3
0.3	145.2
0.4	144.3
0.5	143.7
0.6	143.9
0.7	144.5
0.8	152.4
0.9	160.7

Isothermal decomposition data were obtained at  $\alpha$  values smaller than 0.7 and at temperatures ranging from 68° to 88°C. The data were fitted to a variety of kinetic expressions describing different solid-state decomposition mechanisms

[7]. The linearity of plots (both visually and through the correlation coefficient) of calculated values of  $f(\alpha)$  against time for each kinetic expression was taken as a criterion for identification of the rate equation. Two kinetic equations gave high correlation coefficient values (average values in brackets), i.e. the Avrami-Erofeev equation with  $n = 2$  (0.9959)

$$f(\alpha) = [-\ln(1 - \alpha)]^{1/2};$$

and the Avrami-Erofeev equation with  $n = 3$  (0.9952)

$$f(\alpha) = [-\ln(1 - \alpha)]^{1/3}.$$

The Arrhenius plot (Fig. 3) is obtained using the tempo constant values from the Avrami-Erofeev equation with  $n = 2$ , which seems to be the best fit to the experimental data. From this graph it was calculated that the activation energy,  $E$ , for the first decomposition step is  $148.8 \text{ kJ} \cdot \text{mol}^{-1}$  and  $\ln(A)$  is 42.2.

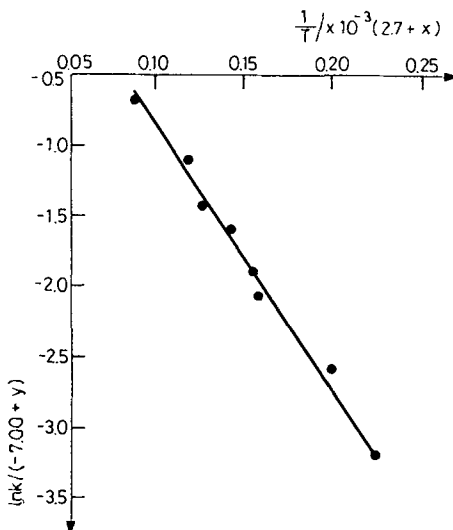
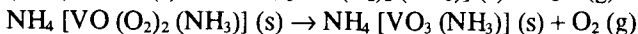
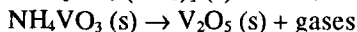
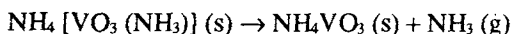


Fig. 3 Arrhenius plot using the isothermal decomposition data for which the Avrami-Erofeev equation, with  $n = 2$  gave the best fit

## Conclusions

The decomposition of ammonium peroxovanadate proceeds via the reactions:





The last reaction proceeds via a number of intermediate reactions, but these are not discussed in this paper.

The first reaction, in which a water molecule is given off, is a single-step reaction, as implied by the independence of the transformation-degree ( $\alpha$ ) to activation energy ( $E$ ). The activation energy of this first step is  $144 \text{ kJ}\cdot\text{mol}^{-1}$ . The Avrami-Erofeev equation, with  $n = 2$ , seems to best describe the kinetics of this decomposition step, and an activation energy of  $148.8 \text{ kJ}\cdot\text{mol}^{-1}$  was calculated using isothermal methods. A  $\ln(A)$  value of 42.2 was determined. The activation energy value of  $148.8 \text{ kJ}\cdot\text{mol}^{-1}$  corresponds well to the value of  $E$  determined using the data from the different heating curves ( $144 \text{ kJ}\cdot\text{mol}^{-1}$ ).

## References

- 1 C. A. Strydom and D. de Waal, *J. Thermal Anal.*, accepted for publication.
- 2 W. W. Wendlandt, *Thermal Analysis*, 3rd Edition, John Wiley & Sons, New York 1985, p. 57.
- 3 S. V. Vyazovkin and A. I. Lesnikovich, *Thermochim. Acta*, 165 (1990) 273.
- 4 D. Dollimore, *Anal. Chem.*, 62 (1990) 44R.
- 5 A. R. Salvador, E. G. Calvo and A. I. Gulias, *Thermochim. Acta.*, 73 (1984) 101.
- 6 K. Nakamoto, 'Infrared and Raman Spectra of Inorganic and Coordination Compounds', John Wiley and Sons, 4th Edition 1986, p. 191.
- 7 P. K. Gallagher and D. W. Johnson, *Thermochim. Acta*, 6 (1973) 67.

**Zusammenfassung** — Bei einer Aufheizgeschwindigkeit von 2 Grad/min zersetzt sich Ammoniumperoxovanadat ( $\text{NH}_4)_4\text{V}_2\text{O}_{11}$  oberhalb  $93^\circ\text{C}$  zu  $(\text{NH}_4)[\text{VO}(\text{O}_2)_2(\text{NH}_3)]$ , was sich oberhalb  $106^\circ\text{C}$  wiederum zu  $(\text{NH}_4)[\text{VO}_3(\text{NH}_3)]$  und anschließend oberhalb  $145^\circ\text{C}$  zu Ammoniummetavanadat zersetzt. Bei weiterem Erhitzen wird oberhalb  $320^\circ\text{C}$  Vanadiumpentoxid gebildet. Die erste Zersetzung verläuft in einem einzigen Schritt, der durch die Avrami-Erofeev-Gleichung mit  $n=2$  am besten beschrieben wird. Bei isothermer Analysenmethode wurde für diese Reaktion eine Aktivierungsenergie von  $148.8 \text{ kJ/mol}$  und ein  $\ln(A)$ -Wert von 42.2 berechnet. Unter Verwendung der dynamischen Aufheizdaten und der Konversionsabhängigkeit der Temperatur bei verschiedenen Aufheizgeschwindigkeiten wurde für die erste Zersetzungsreaktion ein mittlerer Wert von  $144 \text{ kJ/mol}$  berechnet.