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Preparation and Studies of a New Ammonium Vanadium Bronze, $(NH_4)_xV_2O_5$

T. PALANISAMY, J. GOPALAKRISHNAN, AND M. V. C. SASTRI*

Department of Chemistry, Indian Institute of Technology, Madras-600036, India

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A new bronze-type phase of composition $(NH_4)_{0.40\pm0.02}V_2O_5$ is obtained around 230°C during the thermal decomposition of NH_4VO_3 in hydrogen atmosphere. The bronze intermediate is characterized by X-ray diffraction, electrical conductivity, magnetic susceptibility, and ESR studies. It is found to be isostructural with other known β-type vanadium bronzes of general formula $M_xV_2O_5$, where M is usually a monovalent metal. Electrical conductivity and magnetic studies indicate the localized character of conduction electrons at V^{+4} sites. At high temperatures (>400°C), the bronze undergoes decomposition and subsequent reduction to V_2O_3 in hydrogen atmosphere.

Introduction

The oxygen bronzes of transition metals, M_xTO_n, where M is usually an alkali metal and T is a transition metal like Ti, V, Mo, W, etc., exhibit interesting structural, electrical, and magnetic properties (*1–4*). It is generally established that in these compounds, the metal M, inserted into the tunnels of the covalent oxide lattice, TO_n, undergoes ionization to supply its valence electron to the transition metal oxide. Of the various transition metal oxides that form bronzes, tungsten bronzes, M_xWO_3, are well known (*1*, *2*). Although both tungsten and vanadium bronzes are conceptually similar, there are marked differences in their properties; while the tungsten bronzes are metallic conductors with weak (Pauli) paramagnetism, the vanadium bronzes are semiconductors exhibiting Curie–Weiss paramagnetic behaviour. The difference in behaviour is explained on the basis of the assumption that in tungsten bronzes, the conduction electrons are placed into an otherwise empty band formed by the overlap of metal t_{2g}–oxygen p_π orbitals, whereas in vanadium bronzes, the valence electron of M is said to be trapped by V_2O_5 matrix to give localized V^{4+} centers (*3*, *4*).

Recently, an ammonium tungsten bronze, $(NH_4)_xWO_3$, has been reported to be formed during the thermal decomposition of ammonium paratungstate in hydrogen atmosphere (*5*). In the present work, the thermal decomposition of NH_4VO_3 is studied in hydrogen atmosphere with a view to finding out whether a similar ammonium vanadium bronze is obtained in this system. The decomposition products are characterized by X-ray diffraction electrical conductivity, magnetic susceptibility, and ESR measurements.

Experimental

NH_4VO_3 (>99.5%) used in this work was supplied by Reanal, Hungary. All other chemicals employed were of BDH AnalaR grade.

The reduction of ammonium metavanadate in hydrogen was followed thermogravimetrically using a Cahn RG Electrobalance. The weight loss suffered by ~100 mg of the sample was recorded continuously while the furnace was heated at a constant rate (10°C/min). The DTA curve in hydrogen was recorded with a Netzsch apparatus (Netzsch Geratebau GmbH, Selb, West Germany) employing Pt crucibles and Pt–Pt/Rh thermocouples at a heating rate of 10°C/*min* (Fig. 1).

The intermediate decomposition product was prepared by heating about 3 g of NH_4VO_3 for 3 hr in hydrogen atmosphere at 230°C. The ammonia content of this intermediate was determined by Kjeldahl method. The total vanadium and lower valence vanadium in the intermediate phase was determined by a potentiometric titration method using Ce(IV) as oxidant.

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* To whom all enquiries should be addressed.

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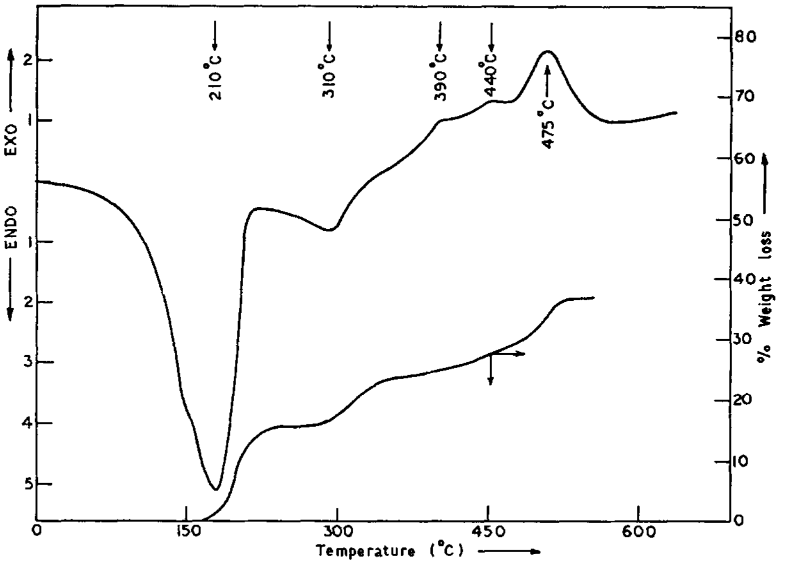

FIG. 1. DTA and TG curves of NH_4VO_3 in hydrogen atmosphere.

For this, a weighed quantity of the sample was treated with a known excess of Ce(IV) solution in $2N \cdot H_2SO_4$. After dissolution, the contents were titrated against standard Fe(II) solution. First, excess Ce(IV) reacted, giving an inflection in the potential, from which vanadium present in the lower valence state was evaluated. Continuing the titration further gave a second inflection corresponding to the end point of the reaction of vanadium(V) with Fe(II). From the second end point, percentage of total vanadium in the sample was calculated. The analytical results are:

	Found (%)	Calcd % for $(NH_4)_{0.38}V_2O_5$
NH_3	3.50	3.42
V^{4+}	10.13	10.26
Total V	53.70	53.96

X-ray powder diffractogram of the intermediate $(NH_4)_{0.38}V_2O_5$ was recorded using Ni-filtered Cu$K\alpha$ radiation. The d spacings and relative intensities of the diffraction lines are given in Table I. The magnetic susceptibility was determined in the temperature range 150–300°K using a Gouy apparatus similar to the one described by Hyde (*6*). Diamagnetic corrections were read from Selwood (*7*) except for O^{2-}, for which a value of -9.8×10^{-6} cgs units was employed (*8*). The sample was pressed into a pellet (1.3 cm diam and 0.8 cm height at a pressure of 65 kg/cm^2, and the electrical

TABLE I

X-RAY DIFFRACTION DATA FOR THE INTERMEDIATE PHASE, β-$(NH_4)_{0.38}V_2O_5$

I_{obsd}	d_{obsd} (Å)	d_{calcd}[a] (Å)	$h\,k\,l$
78	9.67	9.67	1 0 0
33	7.44	7.42	0 0 2
100	7.10	7.09	1 0 1
9	4.86	4.86	2 0 $\bar{2}$
27	4.67	4.83	2 0 0
25	4.12	4.20	2 0 1
18	3.51	3.54	2 0 2
36	3.460	3.480	0 1 1
35	3.427	3.401	3 0 $\bar{2}$
9	3.255	3.224	3 0 0
15	3.175	3.196	1 1 1
31	3.116	3.133	1 0 4
13	2.921	2.934	1 1 2
18	2.858	2.877	2 1 0
9	2.637	2.651	2 0 2
9	2.462	2.463	3 1 $\bar{1}$
8	2.380	2.385	3 0 $\bar{6}$
6	2.338	2.358	1 1 4
6	2.298	2.285	0 1 5
4	2.166	2.142	3 1 $\bar{5}$
10	2.058	2.093	2 1 $\bar{6}$
5	1.985	1.973	3 1 3
4	1.933	1.934	5 0 0
6	1.841	1.841	5 0 1
16	1.804	1.812	3 1 4
8	1.765	1.760	1 2 0
4	1.701	1.701	4 1 3
4	1.595	1.612	3 1 5

[a] Indexed on the basis of a monoclinic cell with $a = 10.26$ Å, $b = 3.58$ Å, $c = 15.75$ Å, and $\beta = 109.5°$.

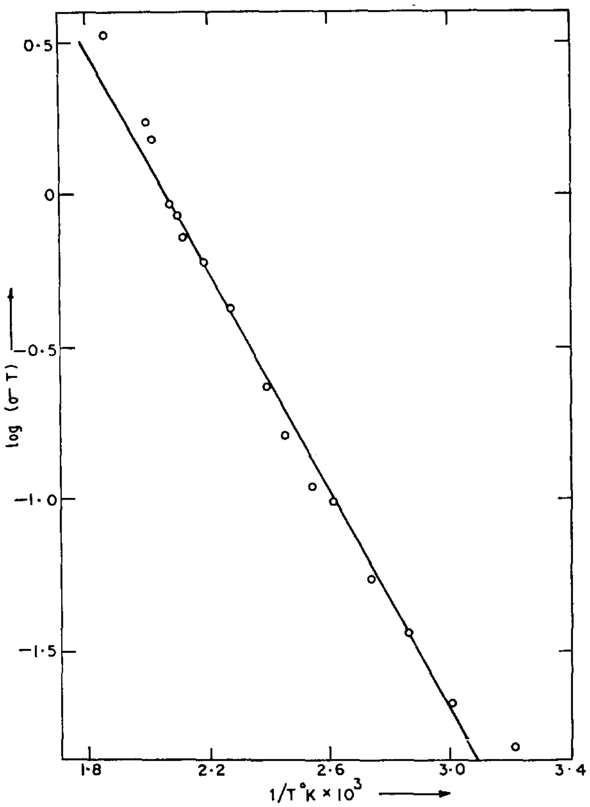

FIG. 2. Electrical conductivity of $(NH_4)_{0.38}V_2O_5$.

conductivity of the pellet between 300–525°K was measured in vacuum (~1 mm Hg) by the two-probe method. The linear plot of $\log(\sigma T)$ vs $1/T$ is given in Fig. 2. Electron spin resonance spectrum of the polycrystalline sample was recorded at room temperature using a Varian E4 EPR spectrometer.

Results and Discussion

Previous studies (*9–16*) on the thermal decomposition of NH_4VO_3 carried out in air, oxygen, vacuum, nitrogen, argon and ammonia have indicated the formation of two intermediates, $(NH_4)_2V_6O_{16}$ and $(NH_4)_2V_4O_{11}$, in the temperature range 180–300°K. The intermediate subsequently decomposes to yield a vanadium oxide, the identity of the oxide being dependent on the prevailing atmosphere during decomposition. Thus V_2O_5, V_3O_7, VO_2, and V_2O_3 are obtained as final products, respectively, in air (*9–11*) or O_2 (*12*), vacuum (*15*), ammonia (*14*), and hydrogen (*13*, *16*). Whereas the formation of V_2O_3 as the final product in the decomposition of NH_4VO_3 in hydrogen is well-established (*13*, *16*), the nature of intermediates is not characterized so far.

In the present study, DTA and TG studies of NH_4VO_3 in hydrogen (Fig. 1) indicate the formation of an intermediate phase at 225–230°C. The weight loss observed up to 230°C is 18.5%, whereas the value calculated for the reaction

$$2NH_4VO_3 \rightarrow (NH_4)_{0.4}V_2O_5 + 1.6\,NH_3 + 0.8\,H_2O + 0.1\,O_2$$

is 19.15%. Analysis of the intermediate obtained at 230°C for NH_3, total vanadium, and vanadium(IV), shows that the intermediate compound has the composition $(NH_4)_{0.40\pm0.02}V_2O_5$. The composition of the individual preparations varied between $(NH_4)_{0.38}V_2O_5$ and $(NH_4)_{0.42}V_2O_5$ depending on the duration of heating at 230–235°C. The studies reported in this paper have been carried out with a sample analysing to $(NH_4)_{0.38}V_2O_5$ (prepared by heating about 3 g of NH_4VO_3 in flowing hydrogen at 230°C for 3 hr).

The DTA of NH_4VO_3 shows a sharp endothermic peak at 210–220°C both in air (*17*) and hydrogen. In air, the endotherm is associated with formation of ammonium hexavanadate $(NH_4)_2V_6O_{16}$ as intermediate. This led us to the speculation that, in hydrogen too, the same intermediate might be formed first which may undergo subsequent reduction to form a bronze-type phase, $(NH_4)_xV_2O_5$ with $0.38 \leqslant x \leqslant 0.42$. To test this possibility, ammonium hexavanadate was separately prepared by heating NH_4VO_3 in air around 210°C and its DTA pattern in hydrogen recorded. The latter did not reveal any endothermic effect in the temperature range 200–300°C, suggesting that NH_4VO_3 does in fact decompose in hydrogen atmosphere first to the hexavanadate which subsequently undergoes reduction to the bronze-type phase.

The X-ray powder diffraction pattern of the bronze $(NH_4)_{0.38}V_2O_5$ shows *d*-spacings and relative intensities which do not compare with any of the known ammonium vanadium oxides (*18*, *19*). The X-ray data are, however, in close agreement with those of *β*-vanadium bronzes, $M_xV_2O_5$ (M = Li, Na, Cu, Ag, etc.) (*20–22*). The observed diffraction lines are indexed on the basis of a monoclinic unit cell with $a = 10.26$ Å, $b = 3.58$ Å, $c = 15.75$ Å, and $\beta = 109.5°$ (Table I). The unit cell parameters compared closely with those of other *β*-vanadium bronzes (*20–22*). On the basis of X-ray diffraction data, a *β*-vanadium bronze structure could therefore be suggested to the phase $(NH_4)_{0.38}V_2O_5$. However, exact position of NH_4^+ ions within the tunnels of V_2O_5 matrix cannot be determined from powder diffraction data alone.

The ESR and magnetic susceptibility measurements indicate presence of V^{4+} ions in the compound. The line width (200*G*) of the signal at room temperature and *g* value (1.962) are characteristic of V^{4+} ions in oxide lattices and compare favorably with the corresponding value of Li- and Na-vanadium bronzes (*23*).

The effective magnetic moment, μ_{eff}, at room temperature per mole of V^{4+} ions in the compound is 1.726 β_B which corresponds closely to the "spin-only" value required for one unpaired electron. The molar susceptibility χ_m follows Curie–Weiss law, $\chi_m = C/(T - \theta)$ in the temperature range 150–300°K with Weiss constant $\theta = -277$°K (Table II). Similar large negative Weiss constants are reported for all *β*-vanadium bronzes (*1*, *2*, *24*). Although such large negative Weiss constants are usually considered indicative of an antiferromagnetic ordering, no such behaviour was found in *β*-$Li_xV_2O_5$, even at liquid helium temperature (*24*). It has been suggested (*3*, *24*) that the strong covalent interaction between V $3d_\pi$–O $2p_\pi$–V $3d_\pi$ orbitals may be responsible for the negative Weiss constant and reduction of μ_{eff} at low temperatures. However, contributions from spin-orbit coupling to low-lying excited states (0.02–0.05 eV from the ground state) should be taken into account in interpreting the magnetic properties (*25*).

TABLE II

MAGNETIC SUSCEPTIBILITY DATA OF $(NH_4)_{0.38}V_2O_5$

T (°K)	$\chi_m \times 10^6$ (cgs emu)	μ_{eff} β_B
302	1233	1.726
276	1235	1.650
260	1286	1.635
239	1340	1.600
219	1393	1.562
202	1446	1.528
185	1500	1.489
168	1658	1.493

Electrical conductivity measurements reveal semiconducting (*n*-type) behaviour for the phase $(NH_4)_{0.38}V_2O_5$. The conductivity at room temperature of the pelletized polycrystalline sample is 3×10^{-5} ohm^{-1} cm^{-1}. It has been shown (*26–28*) that, according to the "small-polaron" model, the electrical conductivity of a single carrier system such as vanadium bronzes is given by

$$\sigma \sim (ne^2a^2/kT)\exp(-E/kT)$$

and

$$\mu = (ea^2/kT)\exp(-E/kT),$$

where n is the charge carrier concentration, μ its mobility, and a the jump distance during hopping. n is essentially a constant in the temperature range studied (300–550°K), as all the donor (V^{4+}) centers are expected to ionize at this fairly high temperature. Therefore, any activation energy observed for σ would arise only from the thermally activated mobility of the charge carriers. For such a case, a plot of $\log(\sigma T)$ versus $1/T$ is expected to be linear. The experimental data (Fig. 2) show that it is indeed the case with $(NH_4)_{0.38}V_2O_5$. However, the observed

TABLE III

X-RAY DIFFRACTION DATA OF THE FINAL DECOMPOSITION PRODUCT OF NH_4VO_3 IN HYDROGEN ATMOSPHERE OBTAINED AT ~550°C

d_{obsd} (Å)	I_{obsd}	$d_{reported}$[a] (Å)	$I_{reported}$
3.663	40	3.65	60
2.722	72	2.70	80
2.481	80	2.47	60
2.186	45	2.18	20
1.828	48	1.83	25
1.698	100	1.69	100
1.551	16	1.57	3
1.471	25	1.47	25
1.429	40	1.43	30

[a] Values reported for V_2O_3 in ASTM card No. 1-1293.

activation energy (~0.3 eV) is higher than the value usually reported (~0.1 eV) for other alkali vanadium bronzes (*1*, *2*, *28*). The high resistivity and activation energy is most probably due to the polycrystalline nature of the sample employed in the present work.

Nature of the Final Product of Decomposition

The intermediate bronze, $(NH_4)_xV_2O_5$, undergoes exothermic decomposition and reduction in the temperature range 400–480°C (Fig. 1). The total weight loss observed in the TG curve is 35.6% while the value calculated for the overall reaction

$$2NH_4VO_3 + 2H_2 \rightarrow V_2O_3 + 2NH_3 + 3H_2O$$

is 35.9%. Chemical analysis of V(III) and X-ray diffraction of the final product confirm it to be V_2O_3 (Table III).

Conclusion

A β-type ammonium vanadium bronze, $(NH_4)_{0.40\pm0.02}V_2O_5$, is obtained as an intermediate in the decomposition of NH_4VO_3 in hydrogen atmosphere at 230°C. The electrical conductivity, ESR, and magnetic susceptibility studies indicate the localized nature of V^{4+} centers in the compound. Above 400°C, the bronze undergoes decomposition and further reduction in hydrogen to yield V_2O_3 as the final product.

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References

1. P. HAGENMULLER, *in* "Progress in Solid State Chemistry" (H. Reiss, Ed.), Vol. 5, pp. 71–144. Pergamon, London, 1970.

2. P. HAGENMULLER, *in* "The Chemistry of Extended Defects in Non-metallic Solids" (L. Eyring and M. O'Keeffe, Eds.), pp. 91–108. North-Holland, Amsterdam, 1970.

3. M. J. SIENKO, *in* "The Alkali Metals" pp. 429–451, Special Publication No. 22. The Chemical Society, London, 1967.

4. J. B. GOODENOUGH, *in* "Progress in Solid State Chemistry" (H. Reiss, Ed.), Vol. 5, pp. 367–376. Pergamon, London, 1970.

5. P. G. DICKENS, A. C. HALLIWELL, D. J. MURPHY and M. S. WHITTINGHAM, *Trans. Faraday Soc.* **67**, 794 (1971).

6. K. E. HYDE, *J. Chem. Educ.* **49**, 69 (1972).

7. P. W. SELWOOD, "Magnetochemistry" (P. W. Sellwood, Ed.), 2nd Ed., p. 78. Wiley Interscience, New York, 1956.

8. M. J. SIENKO AND B. BANERJEE, *J. Amer. Chem. Soc.* **83**, 4149 (1961).

9. J. TRAU, *Rocz. Chem.* **36**, 1365 (1962).

10. J. TRAU, *Zesz. Nauk. Politech. Krakow. Mech.* **21**, 113 (1966).

11. J. LAMURE and G. COLLIN, *C. R. Acad. Sci. Paris* **258**, 6433 (1964).

12. M. TANIGUCHI AND T. R. INGRAHAM, *Can. J. Chem.* **42**, 2467 (1964).

13. T. SATA, E. KOMADA, AND Y. ITO, *Kogyo Kagaku Zasshi* **71**, 643 (1968).

14. M. E. BROWN AND B. V. STEWART, *J. Thermal Anal.* **2**, 287 (1970).

15. IL-HYAN PARK, *J. Korean Chem. Soc.* **16**, 157 (1972).

16. M. KATO, M. TANIGUCHI, AND T. KUBO, *Kogyo Kagaku Zasshi* **69**, 2102 (1966).

17. L. ERDEY, S. GAL, AND G. LIPTAY, *Talanta* **11**, 913 (1964).

18. A. DESCHANVRES, G. NOUET, AND B. RAVEAU, *C. R. Acad. Sci. Paris* **261**, 3144 (1965).

19. A. D. KELMERS, *J. Inorg. Nucl. Chem.* **21**, 45 (1961).

20. A. HARDY, J. GALY, A. CASALOT, AND M. POUCHARD, *Bull. Soc. Chim. Fr.* **4**, 1056 (1965).

21. A. CASALOT, A. DESCHANVRES, P. HAGENMULLER, AND B. RAVEAU, *Bull. Soc. Chim. Fr.* **6**, 1730 (1965).

22. A. Casalot and M. Pouchard, *Bull. Soc. Chim. Fr.* **10**, 3817 (1967).
23. J. Gendell, R. M. Cotts, and M. J. Sienko, *J. Chem. Phys.* **37**, 220 (1962).
24. H. Kessler and M. J. Sienko, *J. Solid State Chem.* **1**, 152 (1970).
25. J. B. Goodenough, private communication.
26. T. Holstein, *Ann. Phys. (New York)* **8**, 343 (1959).
27. L. Friedman, *Phys. Rev.* **135**, A233 (1964).
28. J. H. Perlstein and M. J. Sienko, *J. Chem. Phys.* **48**, 174 (1968).