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THERMAL DECOMPOSITION OF TETRAMETHYLAMMONIUM DI-μ-FLUOROBIS[AQUADIFLUORO-OXOVANADATE(IV)]

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ABSTRACT

Thermal decomposition of $[NMe_4]_2[V_2O_2F_6(H_2O)_2]$ has been investigated by simultaneous TG, DTG and DTA. Measurements have been carried out in a dynamic atmosphere of dry air and argon, respectively. Intermediate phases and final products have been characterized by X-ray powder and infrared spectroscopy. Thermal decomposition in argon is accomplished in three steps. In the first water is given off, the second and the third ones, however, overlap, and the stoichiometries of the decomposition reactions are not evident from the TG curve. The final product is an impure vanadium trifluoride. Thermal decomposition in air also gives anhydrous compound in the first step. Further pyrolysis is entirely different due to oxidation of tetramethylammonium and of vanadium. The final product of the decomposition is vanadium pentoxide.

INTRODUCTION

Thermal decomposition of numerous fluorometallates has been studied in recent years [1–5] in order to evaluate decomposition reactions and to prepare new inorganic compounds.

An interesting common feature to all fluoro-oxovanadates is the basic octahedral structural unit, usually $[VOF_5]^{3-}$, with the very stable VO^{2+} group, which persists in many reactions in the first coordination sphere of vanadium. Tetramethylammonium di-μ-fluoro-*bis*[aquadifluoro-oxovanadate(IV)] consists of dimeric units $[VOF_3(H_2O)_2]_2$ formed by sharing a common edge between the two $[VOF_4(H_2O)]$ octahedra [6].

We report here on the thermal decomposition of this complex, studied in both inert and oxidative environments.

EXPERIMENTAL

The compound was prepared as described elsewhere [6]. TG, DTG and DTA curves were obtained simultaneously by means of a Mettler TA1

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thermoanalyzer with Pt crucibles. Measurements were carried out in dynamic atmospheres (5 l h^{-1}) of dry argon and air, respectively, at a heating rate of 2 K min^{-1} and with sample masses of 100 mg. Inert alumina was used as the reference material for DTA. Intermediate phases were obtained by heating the initial compound to the desired temperatures and cooling down the samples.

Infrared spectra were obtained using a Model 521 Perkin Elmer grating spectrometer (4000–250 cm^{-1}). Crystallographic powder spectra were obtained with a Guinier-de Wolff camera using CuK_α radiation.

RESULTS AND DISCUSSION

Thermal decomposition of the title complex in argon is accomplished in three steps as shown in Fig. 1. The compound begins to lose its water molecules at 110 °C and terminates at 180 °C with a DTG peak at 165 °C. The experimental mass loss of 8.4% agrees with the theoretical value of 8.34%. This first step is very well resolved from the following two. Reversible dehydration gave very hygroscopic anhydrous complex isolated in high-vacuum at 130 °C [6].

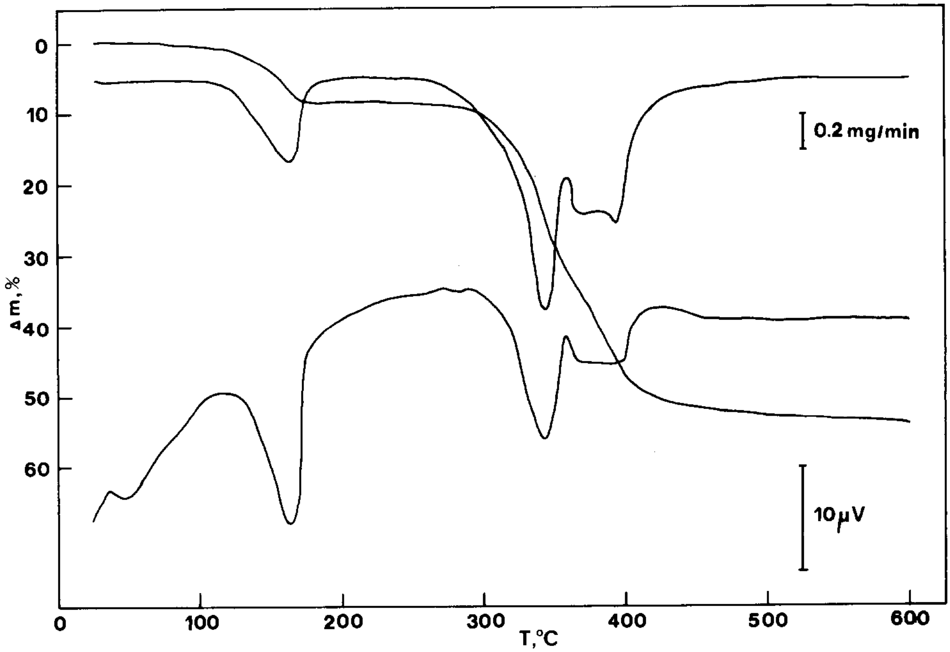

Fig. 1. TG, DTG and DTA curves of $[NMe_4]_2[V_2O_2F_6(H_2O)_2]$ recorded in argon.

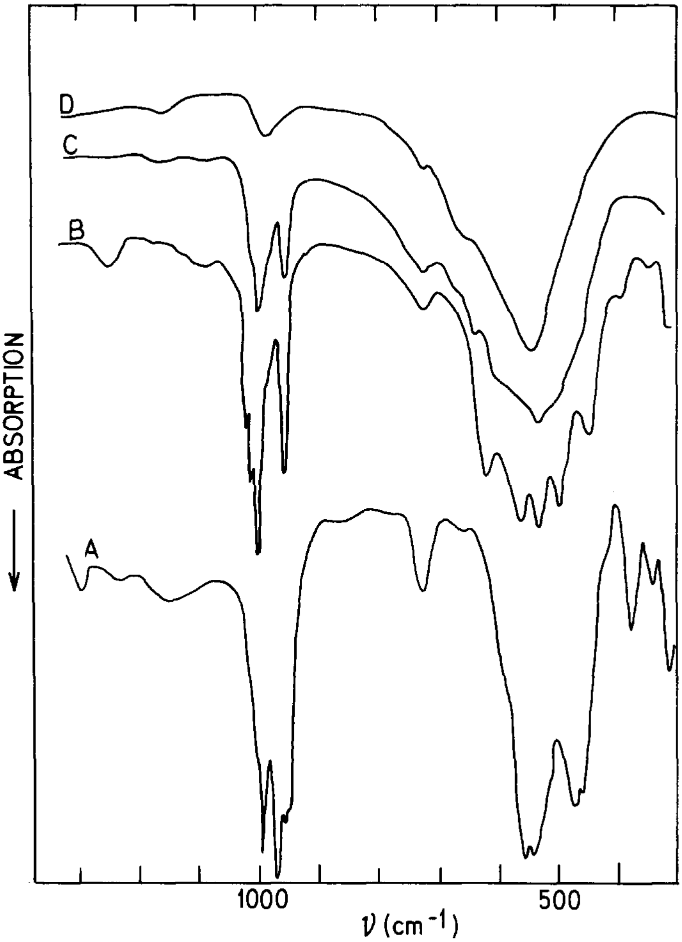

Fig. 2. IR spectra of intermediate phases (A, dehydrate; B, 33.3% mass loss; C, 39.0% mass loss; D, 49.7% mass loss) isolated in argon.

The second and the third steps overlap to such an extent that the TG curve does not give any information about the stoichiometry of the decomposition reactions. In the X-ray powder photograph of the residue, weak and diffuse lines of VF_3 were found. Chemical analysis of the residue (48.9% V, 48.1% F) gave a 1.00: 2.64 V: F ratio. The final product is therefore an impure form of VF_3. The most probable admixture is vanadium(III) oxide which usually appears nonstoichiometric. Analytical data as well as the final mass loss of 52.6% are close to the composition $5VF_3 + 1VO_{1.5}$ with a theoretical weight loss of 52.3%.

The representative part of the IR spectra of the intermediate phases, as well as of the residue, are shown in Fig. 2. The main difference between the IR spectra of the pure dehydrated compound and of the intermediate with 33.3% mass loss, is the disappearance of the 960 cm^{-1} band and intensity

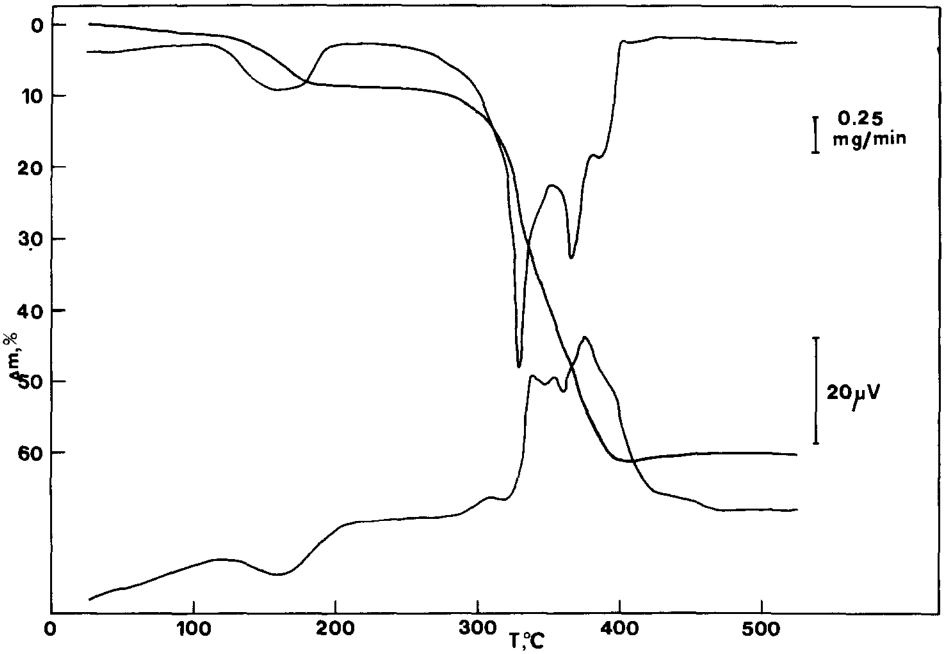

Fig. 3. TG, DTG and DTA curves of $[NMe_4]_2[V_2O_2F_6(H_2O)_2]$ recorded in air.

diminution of the 950 cm^{-1} band. As the two bands belong to $N(CH_3)_4$ [6], the spectrum indicates a reduced amount of the cation present. In the X-ray powder pattern there are only weak lines, but the majority of them belong to the initial complex. The structure of the dehydrate, which turns to hydrate on cooling in air, is therefore preserved, at least partially, up to about 360 ° C, where the second step of the decomposition finishes, as shown on the DTG curve.

The next intermediate (39.0% mass loss) is amorphous. Its IR spectrum changes considerably. The bands between 450 and 615 cm^{-1} combine to a broad band which is characteristic of VF_3 [7]. On the other hand, there is a diminution in intensity of 950 (ν_{NMe_4}) and of 988 ($\nu_{V=O}$) bands [6]. Both features account for reduction of V(IV) to V(III). The IR spectrum of the final product is very close to that reported for VF_3.

Thermoanalytical curves for the decomposition in air are presented in Fig. 3. The first step, dehydration, is the same as in argon. Further decomposition, however, is entirely different with V_2O_5 as the end product, as proved by X-ray powder and IR spectra, respectively. The final mass loss is 59.4%, in agreement with the calculated value of 58.0%. Decomposition of the dehydrated complex commences at the same temperature as in argon, but the reaction is exothermic and can be ascribed to oxidative pyrolysis of the tetramethylammonium ion. The IR spectrum of the intermediate phase (28.5% mass loss, Fig. 4) is similar to that obtained in argon. By increasing

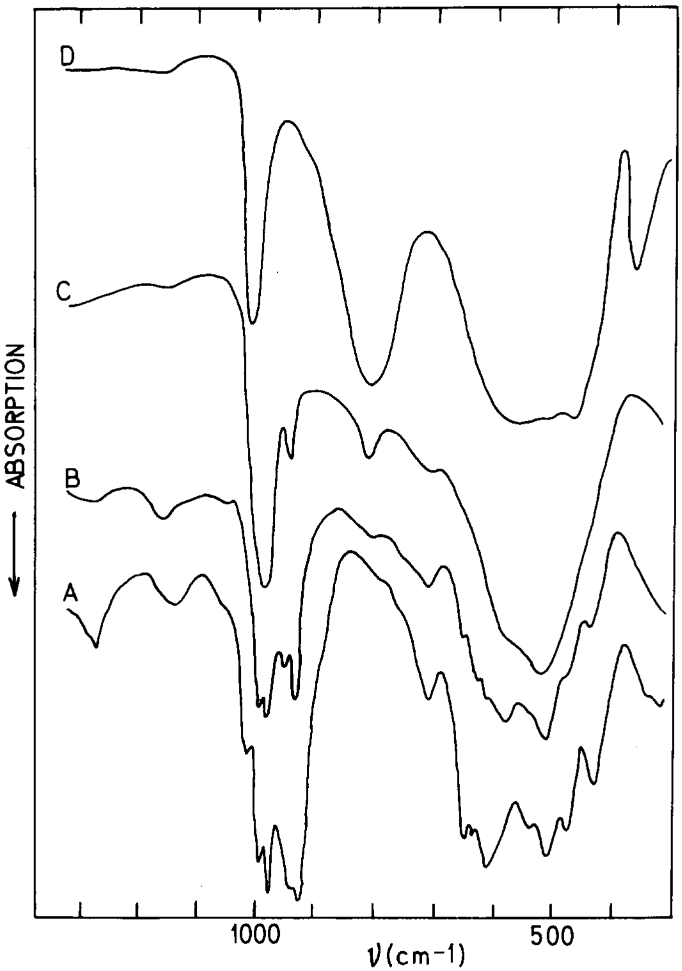

Fig. 4. IR spectra of intermediate phases (A, 28.5% mass loss; B, 36.9% mass loss; C, 47.0% mass loss; D, 59.4% mass loss) isolated in air.

the temperature, the V_2O_5 [8] band at 825 cm^{-1} appears, indicating the oxidation of vanadium. In the IR spectrum of the last intermediate (47.0% mass loss) the bands at 950 and 820 cm^{-1} reveal that both reactions, decomposition of the cation and oxidation of the vanadium, procede simultaneously, resulting in a rather complicated process, as shown on the DTA curve, which is exothermic throughout. The terminal weight gain on TG indicates the final oxidation of vanadium.

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REFERENCES

1 B.I. Sturm and C.W. Sheridan, in J. Kleinberg (Ed.), Inorganic Synthesis, Vol. 7, McGraw-Hill, New York, 1963, p. 87.
2 B.I. Sturm, Inorg. Chem., 1 (1962) 665.
3 P. Bukovec and J. Šiftar, in H.G. Wiedemann (Ed.), Thermal Analysis, Vol. 2, Birkhauser, Basel, 1972, p. 321.
4 P. Bukovec and J. Šiftar, Thermochim. Acta, 21 (1977) 117.
5 A. Demšar and P. Bukovec, Thermochim. Acta, 92 (1985) 665.
6 P. Bukovec, S. Milićev, A. Demsar and L. Golic, J. Chem. Soc., Dalton Trans., (1981) 1802.
7 R.G. Cavell and H.C. Clark, Inorg. Chem., 3 (1964) 1789.
8 R.A. Nyquist and R.O. Kagel, Infrared Spectra of Inorganic Compounds, Academic Press, New York, 1971, p. 217.