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THERMAL DECOMPOSITION OF TETRAETHYLAMMONIUM FLUOROOXOVANADATES(IV)

A. DEMŠAR and P. BUKOVEC
Department of Chemistry and Chemical Technology, University Edvard Kardelj, 61000 Ljubljana (Yugoslavia)

ABSTRACT

Thermal decomposition of $|N(C_2H_5)_4|_2|V_2O_2F_2(H_2O)_2|$ and $|N(C_2H_5)_4||V_2O_2F_5(H_2O)_3|$ has been investigated by simultaneous TG, DTG, and DTA. Measurements have been carried out in a dynamic atmosphere of dry argon and air respectively. Intermediate phases and final products have been characterized by X-ray powder and infrared spectroscopy. $|N(C_2H_5)_4|_2|V_2O_2F_6(H_2O)_2|$ is dehydrated in the first step, which is followed by melting. The final product is an impure VF_3 in argon and V_2O_5 in air respectively. Thermal decomposition of $|N(C_2H_5)_4||V_2O_2F_5(H_2O)_3|$ also gives anhydrous compound in the first step. Further pyrolisis in argon is accomplished in two overlaping steps. The final product of decomposition is an impure VF_3. The decomposition of anhydrous product in air is exothermic due to oxidation of tetraethylammonium cation and vanadium with V_2O_5 as final residue.

The role of the cation in thermal decomposition of ammonium and tetramethyl- and tetraethylammonium fluorooxovanadates(IV) is discussed.

INTRODUCTION

Thermal decomposition of tetramethylammonium di-μ-fluorobis|aquadifluoro-oxovanadate(IV)| gives anhydrous compound in the first step and an impure vanadium trifluoride as final product of decomposition in argon. In air the dehydration is followed by oxidation to vanadium pentoxide (1).

We report here on the thermal decomposition of fluorooxovanadates(IV) with tetraethylammonium cation.

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EXPERIMENTAL

Synthesis of $|N(C_2H_5)_4|_2|V_2O_2F_2(H_2O)_2|$ was described elsewhere (2). $|(C_2H_5)_4||V_2O_2F_5(H_2O)_3|$ was prepared by isothermal crystallization at room temperature from solutions of $(C_2H_5)_4NF$ and VOF_2 in molar ratio of 1:1 in 5% HF. Blue crystals were filtred and washed with methanol and dried in vacuum desiccator (found 21.39%C, 6.14%H, 3.28%N, 23.9%V, 23.65%F, calculated 23.26%C, 6.35%H, 3.39%N, 24.66%V, 22.99%F).

Thermoanalytical curves were obtained by means of a Mettler TA1 thermoanalyzer. Experimental conditions: TD1 sample holder, platinum crucible, sample weights 100 mg, heating rate of 2°C/min, atmosphere of dry argon and dry air with 5 l/h flow rate. Intermediate phases were obtained by heating the initial compound at a heating rate 6°C/min to desired mass loss and cooling the samples.

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

RESULTS AND DISCUSSION

Thermal decomposition of $|(C_2H_5)_4|_2|V_2O_2F_6(H_2O)_2|$ in argon atmosphere (Fig.1) gives an anhydrous compound in the first step. The reaction takes place between 80 and 150°C with mass loss of 6.4% (calculated 6.62%). On the DTA curve there is another endothermic peak at 180°C, which can be ascribed to melting as shown in a separate experiment. Further decomposition to final residue gives vanadium trifluoride as proved by X-ray powder pattern. Mass loss of 63.9% exceeds the calculated for the decomposition to vanadium trifluoride (57.54%). The difference can be due to the admixture of vanadium(III) oxide in final residue (1). The representative part of IR spectra of the intermediate phases, as well as of the residue, are shown in Fig.2. The spectrum of 32.9% mass loss intermediate is similar to the spectrum of the anhydrous compound. In IR spectrum of the next intermediate (50.5% mass loss) the bands between 450 and 600 cm^{-1} combine to a broad band which is characteristic for VF_3 (3). The diminution of the intensity of ca.1000 cm^{-1} ($\nu_{V=O}$) band takes place in the last step of the decomposition due to reduction of V(IV) to V(III). IR spectrum of the final product is very close to that reported for VF_3.

In the thermal decomposition of $|N(C_2H_5)_4|_2|V_2O_2F_6(H_2O)_2|$ in air dehydration and further decomposition overlap without characteristic DTG and DTA peaks, to final mass loss of 67.6%. Final residue is vanadium pentoxide (calculated 66.99% mass loss) as proved by X-ray powder pattern.

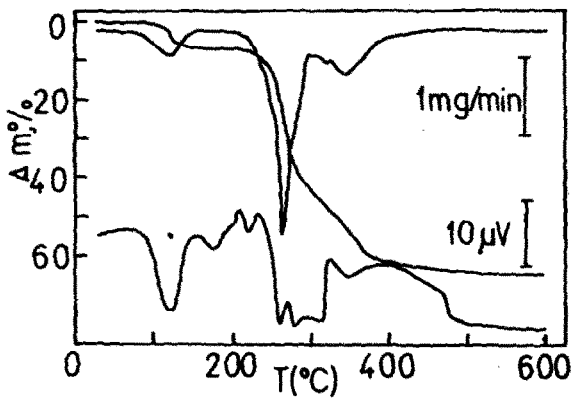

Fig.1 TG, DTG and DTA curves of $|N(C_2H_5)_4|_2|V_2O_2F_6(H_2O)_2|$, recorded in argon

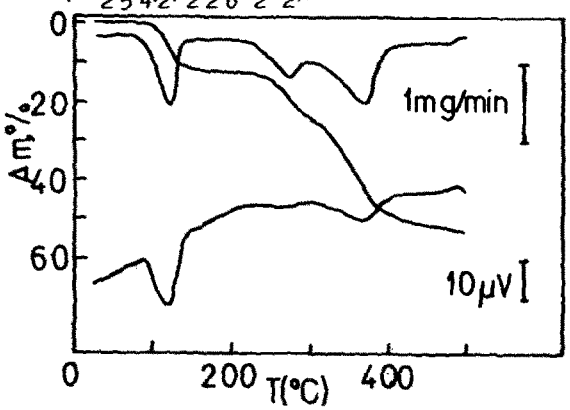

Fig.3. TG, DTG and DTA curves of $|N(C_2H_5)_4||V_2O_2F_5(H_2O)_3|$, recorded in argon

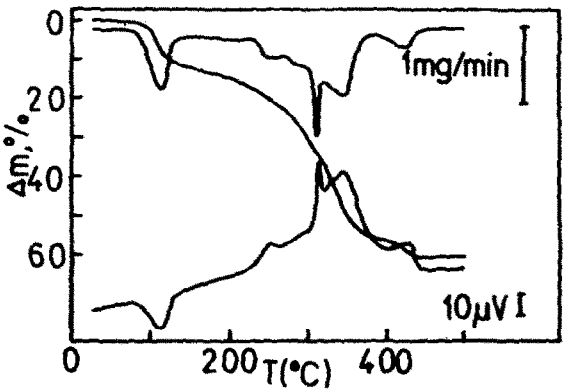

Fig.5. TG, DTG and DTA curves of $|N(C_2H_5)_4||V_2O_2F_5(H_2O)_3|$, recorded in air

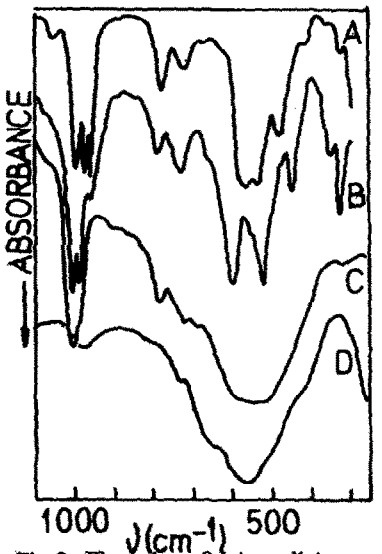

Fig.2. IR spectra of intermediate phases of $|N(C_2H_5)_4|_2|V_2O_2F_6(H_2O)_2|$ (A, dehydrat; B, 32.9% mass loss; C, 50.5% mass loss; D, end residue), isolated in argon

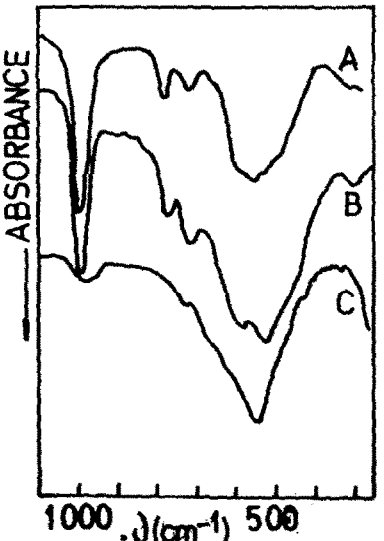

Fig.4. IR spectra of intermediate phases of $|N(C_2H_5)_4||V_2O_2F_5(H_2O)_3|$ (A, dehydrate; B, 34.7% mass loss; C, end residue), isolated in argon

Thermal decomposition of $|N(C_2H_5)_4||V_2O_2F_5(H_2O)_3|$ in argon (Fig.3) begins with dehydratation between 90 and 160°C with mass loss of 12.0% (calculated 13.08%). Anhydrous compound decomposes in two steps. In the X-ray powder pattern of the residue, weak and diffuse lines of VF_3 were found. Chemical analysis of the residue (50.8%V, 36.5% F) gave a 1.00:1.93 V: F ratio. The final product is therefore an impure VF_3, and the most probable admixture vanadium(III) oxide. Analytical data as well as the final mass loss of 53.0% are close to the composition 1.80 VF_3 +1.00 $VO_{1.5}$ with a theoretical weight loss of 53.15%. The representative part of the IR spectra of the intermediate phases, as well as of the residue, are shown in Fig.4. The spectrum of 34.7% mass loss intermediate is similar to the spectrum of the anhydrous compound. The diminution of the intensity of ca. 1000 cm^{-1} ($\nu_{V=O}$) band takes place in the last step of decomposition due to 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 of $|N(C_2H_5)_4||V_2O_2F_5(H_2O)_3|$ in air are shown in Fig.5. The first step, the dehydration, is the same as in argon. The end product of further decomposition is vanadium pentoxide, as proved by X-ray powder pattern. The final mass loss is 60.1% whereas the calculated value for formation of V_2O_5 is 55.98%.

By thermal decomposition of tetramethylammonium (1), ammonium (4) and one of two tetraethylammonium fluorooxovanadates(IV), intermediate phases with VOF_3^- stochiometry of anion are formed. Tetraethylammonium and tetramethyammonium compounds are stable in argon up to 200° and 270°C, respectively. NH_4VOF_3 as an intermediate phase was isolated by the isothermal decomposition of $(NH_4)_2VOF_4$ at 180°C.

REFERENCES

1 A. Demšar and P. Bukovec, Thermochim. Acta, 117(1987)249.
2 A. Demšar and P.Bukovec, Croat. Chem. Acta,57(1984)673.
3 R.G. Cavell and H.C. Clark, Inorg. Chem., 3(1964)1789.
4 A. Demšar and P. Bukovec, Thermochim. Acta, in press