

SYNTHESIS AND THERMAL DECOMPOSITION OF $N_2H_5UO_2(CH_3COO)_3$

Ilinka Donova

*Institute of Chemistry, Faculty of Science, The "Sv. Kiril & Metodij" University,
P. O. Box 162, 91001 Skopje, Republic of Macedonia*

The synthesis of $N_2H_5UO_2(CH_3COO)_3$ is described. The identity of the synthesized compound was confirmed by chemical and infra-red analysis. By means of thermogravimetric, differential thermal analysis and X-ray diffraction, the intermediate and final products of the decomposition were identified. Thermal decomposition of hydrazinium uranyl acetate involves three steps. Two of them are due to decomposition of hydrazinium uranyl acetate to UO_2 , and the third one to the partial oxidation of UO_2 to UO_3 and formation U_3O_8 at higher temperature.

Key words: hydrazinium; uranyl acetate; thermal decomposition; synthesis

INTRODUCTION

There are many data about thermal decomposition of uranyl acetate. Duval [1] has studied the thermal decomposition of uranyl acetate. According to him, uranyl acetate dihydrate is stable up to 100 °C. The water of crystallization is released up to 159 °C. Anhydrous salt is stable from 159 °C to 247 °C. It decomposes slowly at 247 °C, rapidly at 380 °C and explosively at 412 °C.

Kobayashi [2] has also studied the decomposition of uranyl acetate in air. His results do not agree with those of Duval. According to Kobayashi, the uranyl acetate dihydrate releases the water of crystallization between 60 and 120 °C. The anhydrous salt is stable up to 200 °C, when slow decomposition occurs. At 297 °C decomposition is complete. The slight weight increase is observed between 300 and 320 °C. The solid residue is U_3O_8 .

Clough et al. [3] published a detailed and systematized study of thermal decomposition of uranyl acetate in nitrogen and air. The changes in the specific surface area and density during decomposition were studied. Some residues of decomposition were identified, and the kinetics and mechanism of decomposition were suggested.

Yanachkova et al. [4] has studied the thermal decomposition of uranyl acetate, by means of thermo-

gravimetric, differential thermal analysis, X-ray and infra-red method. The intermediate and final products of the decomposition are identified. According to Yanachkova, after dehydration uranyl acetate decomposes to UO_2 it is partially oxidized to UO_3 . The final product, U_3O_8 , is obtained from the interaction of UO_2 with UO_3 in solid state.

The synthesis, powder diffraction data, infra-red, Raman spectra and thermal decomposition of some hydrazinium double sulphates have been studied by several authors [5, 6, 7]. It is also known [5], that during a thermal decomposition of hydrazinium neodymium sulphate monohydrate intermediate ammonium salts are obtained.

In our laboratory [8] we had studied the synthesis and thermal decomposition of M^+ -uranyl acetates, where $M^+ = Li^+, Na^+, K^+, Rb^+, Cs^+$ and NH_4^+ . TG investigations showed that $NH_4UO_2(CH_3COO)_3$ (when the heating was performed in air) decomposes to U_3O_8 , and at DTA measurements (when the heating was performed in the atmosphere of their own pyrolysis products), UO_2 was obtained as a final product.

The aim of this work is the synthesis and thermal decomposition of hydrazinium uranyl acetate.

EXPERIMENTAL

Procedure

The compound was synthesized, by evaporation of the reaction mixture of the uranyl acetate dihydrate

and hydrazine hydrate in molar ratio of $UO_2^{2+} : [N_2H_5]^+ = 1 : 6$ in acetic acid with concentration of 2 mol/dm³. The yellow crystal product was filtered off, washed with water and ethanol and dried in air.

Apparatus and methods

The compound obtained was characterized and investigated by elemental analysis, IR spectroscopy, TG and DTA analysis and X-ray powder diffraction.

The isothermal heating at 200 °C, 400 °C and 600 °C was performed and the X-ray powder diffraction patterns were recorded on the residues of the heating.

Quantitative determinations of C and H were carried out according to Liebig's method on a Coleman Model 33 analyzer and N was determined by the method of Dumas.

Gravimetric method [10] was used for quantitative determination of uranium.

The IR-spectra were recorded on a Fourier transform spectrophotometer Perkin-Elmer in KBr pellets. TG and DTA curves were obtained on a Netzsch thermoanalyser, in dry air in the temperature range from 20 to 800 °C, at a heating rate of 5 °C/min, with α -Al₂O₃ as reference substance and a platinum crucible.

The X-ray powder diffraction patterns were obtained on a Jeol-diffractometer, model JDX-7E, by Cu K- α radiation, Ni-filtered with a goniometer model DX-GO-F.

RESULTS AND DISCUSSION

The results of the quantitative chemical analysis (C, H, N and U) and the mass losses are given, followed by the theoretically values in Table I.

The results show that the synthesized double acetate has the empirical formula, N₂H₅UO₂(CH₃COO)₃. That was confirmed by IR-spectroscopy (Fig. 1).

Table I

Results of the chemical and thermal analysis of N₂H₅UO₂(CH₃COO)₃, in %

	C	H	N	U	Δm to 250 °C	Δm to 360 °C	Δm to 430 °C	Δm to 550 °C	Δm to 825 °C
Exper.	15.11	2.97	5.76	49.49	34.77	42.24	42.24	41.17	41.17
Theoret.	15.01	2.94	5.83	49.57	35.01	43.76	43.76	41.54	41.54

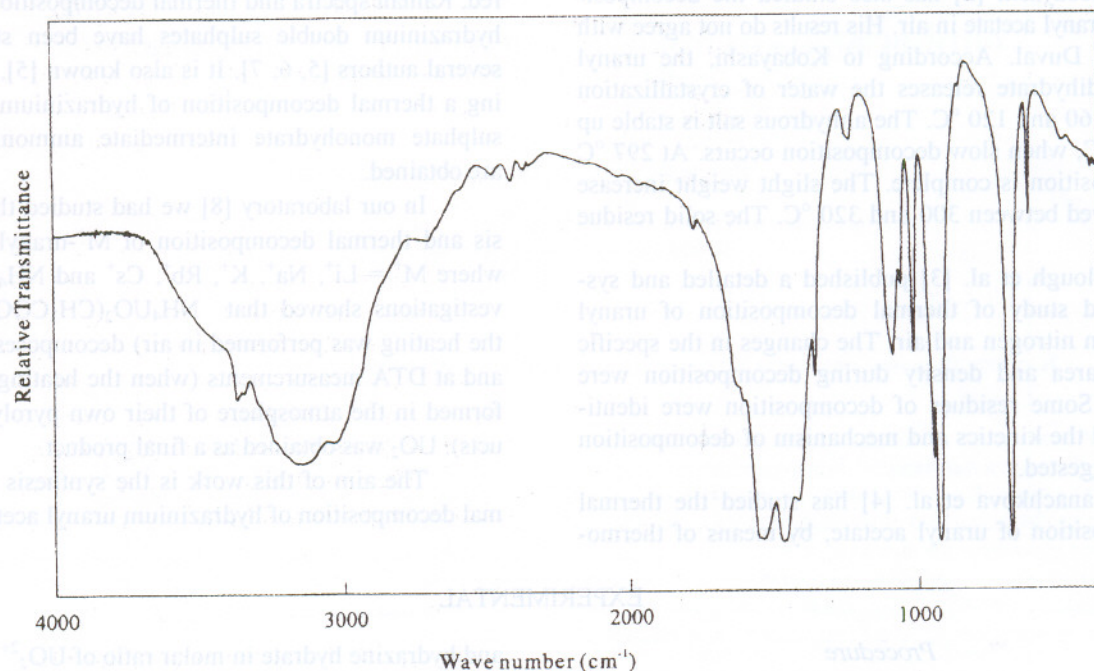


Fig. 1. Infrared spectrum of N₂H₅UO₂(CH₃COO)₃ in KBr pellet

The assignment of the bands from the vibrations of the $N_2H_5^+$, COO^- , UO_2^{2+} ions and CH_3 groups in the infrared spectrum of the title compound are identified by comparison with the literature data [5, 6, 9].

As shown, on Fig. 1, in the $3500-2500\text{ cm}^{-1}$ region of the infrared spectrum there is a broad and complex band with a few shoulders. This band is probably a result of the superposition of the NH stretching vibrations of the $N_2H_5^+$ and antisymmetric and symmetric stretches of the CH_3 groups which appear around 2950 cm^{-1} .

Vibrations are expected in the $1800-1300\text{ cm}^{-1}$ region of bands originating from COO^- and CH_3 . Accordingly, the strong band at 1543 cm^{-1} can be assigned to the COO^- antisymmetric stretch. The two bands at lower frequencies (1465 and 1410 cm^{-1}) are due, probably, to the symmetric stretching COO^- vibration. Namely, the high frequency band, at 1465 cm^{-1} , can be overlapped with the bands originating from antisymmetric bending CH_3 vibrations, while the band around 1353 cm^{-1} can be assigned as a symmetric bending CH_3 vibration.

A weak band which appears around 1235 cm^{-1} is probably a result of the $\delta(NH_3)$. In agreement with the published assignment for various uranyl-acetate compounds [9], the three bands with the frequencies of 1084 , 1055 and 1015 cm^{-1} are assigned as a rocking CH_3 , while a very strong band at the 922 cm^{-1} can be

attributed to the symmetric stretches of the UO_2^{2+} ions. Another intensive band at 680 cm^{-1} as well as a weak one at 615 cm^{-1} we assigned as rocking and wagging COO^- vibrations, respectively.

With the aim to obtain some more information about the thermal stability of the obtained compound, TG and DT analyses were performed.

The thermal decomposition of the $N_2H_5UO_2(CH_3COO)_3$ (Fig. 2), takes place in several steps. In the first step, the compound decomposes to $(NH_4)_2U_2O_7$ in the temperature range from 200 to $250\text{ }^\circ\text{C}$ (calc. value 35.01% , found 34.77%), followed by an endothermic peak at $215\text{ }^\circ\text{C}$. In the second step, in the temperature range from 250 to $360\text{ }^\circ\text{C}$, the compound decomposes, probably, to uran oxides where UO_2 dominate, which is followed by a broad endothermic peak from 250 to $315\text{ }^\circ\text{C}$ (calc. value 43.76% , found 42.24%). From 360 to $430\text{ }^\circ\text{C}$ no changes are observed. The slight weight increase observed between 430 and $550\text{ }^\circ\text{C}$ was supposed to be due to partial oxidation of UO_2 to UO_3 . According to the literature [3, 4], and our results of thermal decomposition, $UO_2 + 2UO_3 = U_3O_8$ (calc. 41.54% , found 41.17%), should be obtained. This reaction is followed by a slight exothermic peak at $525\text{ }^\circ\text{C}$, on the DTA curve.

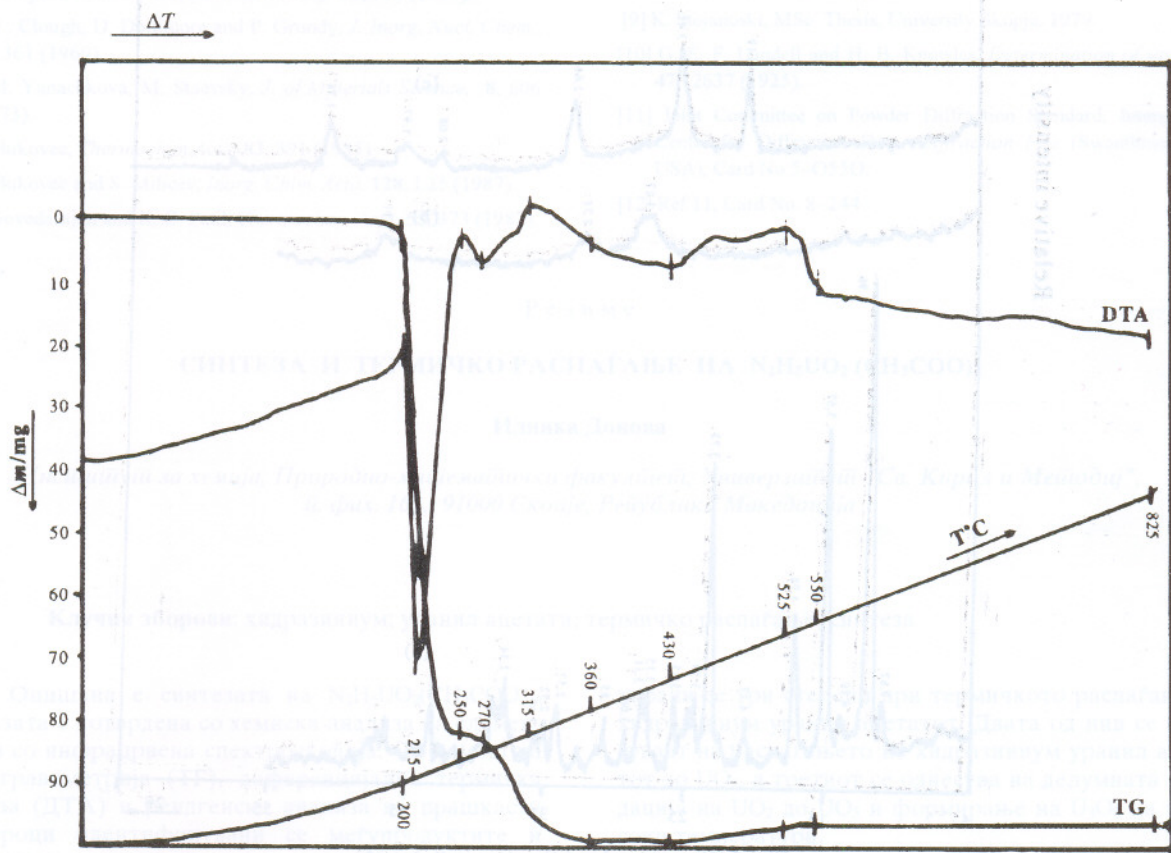


Fig. 2. TG and DTA diagrams of $N_2H_5UO_2(CH_3COO)_3$, $m = 234.4\text{ mg}$

From 550 to 825 °C, only U_3O_8 exists, and the changes are not observed on the TG curve.

Taking into consideration our thermal investigation and literature data [3–5], the possible reaction of thermal decomposition can be expressed as:

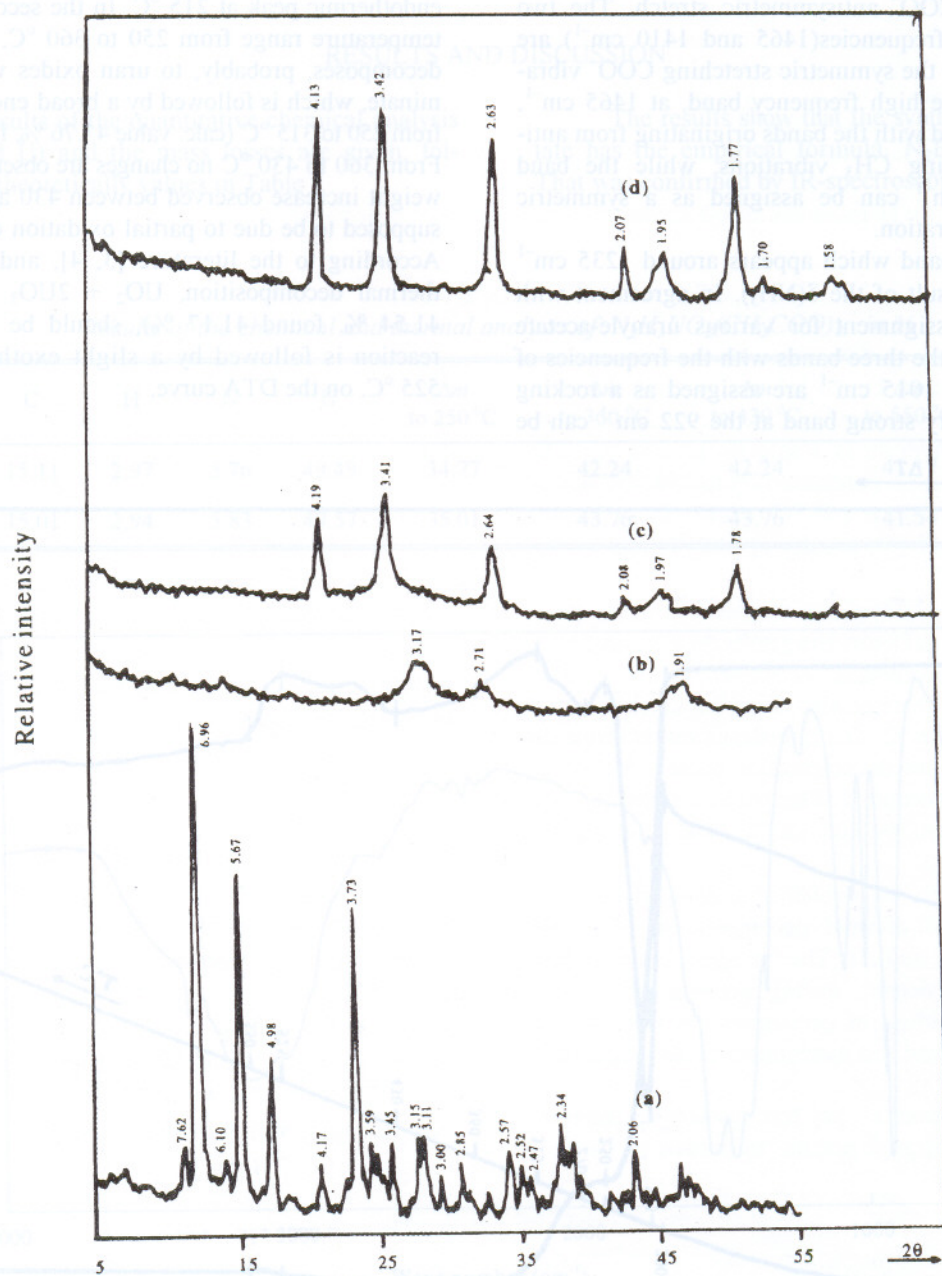
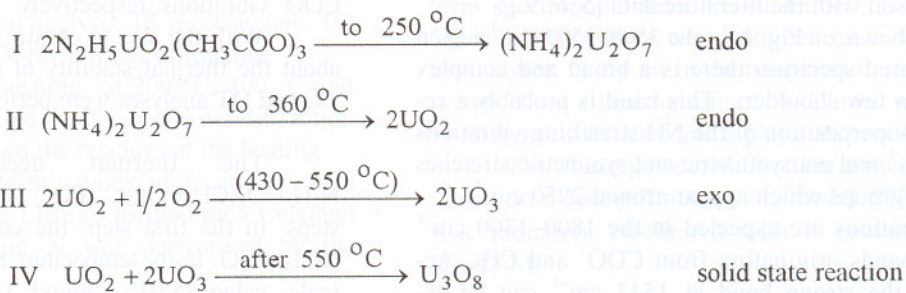


Fig. 3. X-ray powder diffraction patterns of: a) $N_2H_5UO_2(CH_3COO)_3$, b) the residue at 200 °C, c) the residue at 400 °C, d) the residue at 600 °C,

The diffractograms of the initial hydrazinium uranyl acetate and of the products of their thermal decomposition at 200 °C, 400 °C and 600 °C isothermally, are presented on fig.3.

From the X-ray powder diffraction patterns of the initial compound (Fig. 3a), it could be concluded that it is in a crystal form, but, when hydrazinium uranyl acetate was heated at 200 °C for one hour, the crystal substance was transformed into an "amorphous"

state. Only three weak peaks were observed ($d(\text{Å}) = 3.17; 2.71; 1.91$) on the diagram (Fig. 3b), and can be attributed to UO_2 [11]. The obtained diffractograms of the residues of the isothermic heatings at 400 °C and at 600 °C (Fig. 3c and 3d) showed the formation of higher uranium oxide. The d values of both diagrams were in strong agreement with the d value of U_3O_8 ($4.15_x; 3.43_x; 2.64_9; 1.77_6; 3.36_5; 2.61_4; 2.07_4; 1.95_4$) [12].

CONCLUSION

From the results of our investigations it can be concluded that the substance $N_2H_5UO_2(CH_3COO)_3$ can be synthesized by the slow evaporation of a mixture of $UO_2(CH_3COO)_2 \times 2H_2O$ and N_2H_4 in a molar ratio of $UO_2^{2+} : N_2H_5^+ = 1 : 6$, in acetic acid solution. There are three reaction characteristics for the thermal decomposition of $N_2H_5UO_2(CH_3COO)_3$. Two of them respond to decomposition of $N_2H_5UO_2(CH_3COO)_3$ to UO_2 , in temperature interval from 200 °C to 360 °C and the

third one responds to partial oxidation of UO_2 to UO_3 and formation of U_3O_8 to about 550 °C, under dynamic conditions, but at isothermal conditions U_3O_8 is obtained after heating at 400 °C for one hour.

*

Acknowledgments: The author is indebted to Dr Mira Trpkovskaa and MSc Viktor Stefov for their helpful discussions about IR spectrum.

REFERENCES

- [1] C. Duval, *Anal. Chim. Acta*, **20**, 263 (1959).
- [2] I. Kobayshi, *Rika Gaku Kenhushu Hokoky* **36**, 710 (1960).
- [3] P. S. Clough, D. Dollimore and P. Grundy, *J. Inorg. Nucl. Chem.*, **31**, 361 (1969).
- [4] I. M. Yanachkova, M. Staevisky, *J. of Materials Science*, **8**, 606 (1973).
- [5] N. Bukovec, *Thermochim. Acta*, **83**, 391 (1985).
- [6] N. Bukovec and S. Milicev, *Inorg. Chim. Acta*, **128**, L25 (1987).
- [7] S. Govedarajan and K. C. Patil, *Thermochim. Acta*, **55**, 373 (1982).
- [8] I. Donova, *Thermal decomposition of M^+ -uranyl acetate*, MSc. Thesis, University, Skopje, 1981.
- [9] K. Stojanoski, MSc Thesis, University Skopje, 1979.
- [10] G. E. F. Lundell and H. B. Knowles, *Determination of uranium*, **47**, 2637 (1925).
- [11] Joint Committee on Powder Diffraction Standard, International Center for Diffraction Data, *Diffraction File* (Swanhamore, Pa, USA), Card No.5-O550.
- [12] Ref.11, Card No. 8-244.

Резиме

СИНТЕЗА И ТЕРМИЧКО РАСПАЃАЊЕ НА $N_2H_5UO_2(CH_3COO)_3$

Иљинка Донова

Институт за хемија, Природно-математички факултет, Универзитет "Св. Кирил и Методиј",
Ѓ. фах. 162, 91000 Скопје, Република Македонија

Клучни зборови: хидразиниум; уранил ацетати; термичко распаѓање; синтеза

Опишана е синтезата на $N_2H_5UO_2(CH_3COO)_3$. Синтезата е потврдена со хемиска анализа на елементите и со инфрацрвена спектроскопија. Со помош на термогравиметрија (ТГ), диференцијална термичка анализа (ДТА) и рендгенска анализа на прашкасти примероци идентификувани се меѓупродуктите и крајниот продукт на термичкото распаѓање. Конста-

тирани се три степени при термичкото распаѓање на хидразиниум уранил ацетатот. Двата од нив се однесуваат на распаѓањето на хидразиниум уранил ацетатот до UO_2 , а третиот се однесува на делумната оксидација на UO_2 до UO_3 и формирање на U_3O_8 на повиоки температури.