

THERMAL DECOMPOSITION OF URANYL NITRATE HEXAHYDRATE

A thermal analysis – mass spectrometry study

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Abstract

TG-DTA-EGA studies have shown that anhydrous uranyl nitrate cannot be obtained by thermal decomposition of uranyl nitrate hexahydrate. Hydrolysis and polymerization of the salt during dehydration resulted in hydroxynitrates which decomposed in multiple steps with the evolution of oxides of nitrogen and water. The extent of hydrolysis depended on the sample size, heating rate and nature of sample containment. Large samples on decomposition at relatively high heating rates showed evolution of nitric oxide even above 500°C. Infrared studies on the residues prepared at various temperatures supported the conclusions.

Keywords: hydrolysis, polymerization, TG-DTA-EGA, uranyl nitrate hexahydrate

Introduction

Uranyl nitrate is one of the precursors used for the production of nuclear fuels and its thermal decomposition characteristics are of considerable interest. Although a number of studies have been reported [1–4] on the decomposition reaction, there appears to be some controversy regarding the formation of anhydrous uranyl nitrate. While Ondrejcin and Garrett [1] reported $\text{UO}_2(\text{OH})\text{NO}_3$ as an intermediate in the dehydration and decomposition of $\text{UO}_2(\text{NO}_3)_2 \cdot 2\text{H}_2\text{O}$ in vacuum and at atmospheric pressure, Smith [4] reported that $\text{UO}_2(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, $\text{UO}_2(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$ and $\text{UO}_2(\text{NO}_3)_2 \cdot 2\text{H}_2\text{O}$ all dehydrated in multiple steps to give anhydrous uranyl nitrate at about 180°C. Lodding and Ojamaa [3] also reported that uranyl nitrate hexahydrate and uranyl nitrate dihydrate dehydrated in multiple steps to give anhydrous uranyl nitrate at about 210–220°C. However, according to Weigel [5], it is not possible to prepare anhydrous uranyl nitrate by thermal decomposition of $\text{UO}_2(\text{NO}_3)_2 \cdot x\text{H}_2\text{O}$. Woodhead *et al.* [6] observed the presence of polynuclear and nitrate complexes in the melt obtained by heating $\text{UO}_2(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ at 70–80°C. These authors as well as Åberg [7] reported ex-

tensive hydrolysis and polymerization in aqueous solutions of uranyl nitrate when NO_3^- to UO_2^{2+} ratio was favourable. Addison *et al.* [8] reported formation of polynuclear nitrates during the thermal decomposition of anhydrous uranyl nitrate prepared by reacting UO_3 with N_2O_4 . We have carried out a simultaneous TG-DTA-EGA study on the dehydration and decomposition of uranyl nitrate hexahydrate. EGA curves have been obtained by using a quadrupole mass spectrometer coupled to the thermal analyser. The results of this study are presented here.

Experimental

Uranyl nitrate hexahydrate was prepared by the method reported by Livia *et al.* [9]. UO_3 was dissolved in 3M nitric acid at $75^\circ\text{--}80^\circ\text{C}$. After one hour the solution was filtered, concentrated and crystallised. The uranyl nitrate hexahydrate crystals were separated by vacuum filtration, recrystallised, dried in air and stored in a desiccator. The uranium and nitrate contents of the dried sample were determined by standard gravimetric and volumetric methods and were within 1.5% of the theoretical values for $\text{UO}_2(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$.

The experimental set-up used for TG-DTA-EGA measurements is described elsewhere [10]. Sample weights were varied in the range of 50–200 mg. Experiments with each initial weight of the sample were carried out at the heating rates of 2, 5 and $10 \text{ deg}\cdot\text{min}^{-1}$ under an argon flow of 35 ml/min. EGA measurements were carried out for the evolution of NO ($m/e = 30$), NO_2 ($m/e = 46$), O_2 ($m/e = 32$) and H_2O ($m/e = 18$). A Cahn RG Electrobalance, described elsewhere [11], was used to carry out TG measurements on 10 mg samples.

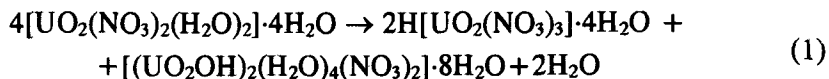
Results and discussion

The TG-DTA-EGA curves for the dehydration and decomposition of uranyl nitrate hexahydrate are presented in Figs 1–3. It is evident from Fig. 3 that the peaks for water loss and loss of NO and NO_2 overlap above 225°C . This result clearly established that uranyl nitrate hexahydrate started to decompose even before the complete removal of its water of crystallization. The analysis of weight loss steps, prior to the temperature of initiation of NO evolution, indicated that only four to five molecules of water of crystallization were lost before the inception of decomposition. Furthermore, the evolution pattern of water as well as the nature of DTA peaks and weight loss steps, unlike those reported by Smith [4], indicated stability of intermediate hydrates with either fractional molecules of water of crystallization or coordinated hydroxyl groups in a polynuclear environment.

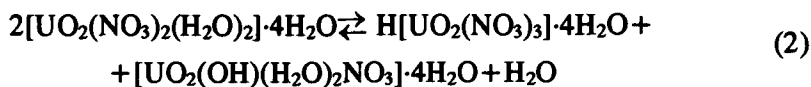
A TG curve (10.45 mg, heating rate: $10.5 \text{ deg}\cdot\text{min}^{-1}$) recorded with a Cahn Electrobalance, using a shallow sample pan, is also included in Fig. 1. It is evident from this figure that the initial sample weight, heating rate and nature of containment of the sample affect significantly the nature of intermediates resulting from the dehydration reaction. This points to extensive hydrolysis accompanied by polymerisation of the products [6], the extent of hydrolysis and polymerisation being dependent on the experimental conditions which affect the contact time of water vapour and the residual hydrates.

Lodding and Ojamaa reported that $\text{UO}_2(\text{NO}_3)_2\cdot 6\text{H}_2\text{O}$ melts at 65°C . Woodhead *et al.* [6] also pointed out that $\text{UO}_2(\text{NO}_3)_2\cdot 6\text{H}_2\text{O}$ was in a molten state when heated to $70\text{--}80^\circ\text{C}$. In our experiments, the simultaneous TG-DTA curves recorded for uranyl nitrate hexahydrate weighing 51.3 mg (Fig. 1) at the heating rate of $2 \text{ deg}\cdot\text{min}^{-1}$ indicated that the peak temperature for the DTA curve in the temperature range of $25\text{--}80^\circ\text{C}$ was at 70°C . The corresponding TG curve showed a constant weight plateau in the temperature range of $68\text{--}72^\circ\text{C}$. Furthermore, the DTA peak appeared to have a shoulder at 60°C . These features of the TG-DTA curves may be indicative of melting of the composition present in the temperature range of $60\text{--}70^\circ\text{C}$. However, cooling curves recorded after heating about 50 mg of the sample in the thermal analyser to $70\text{--}75^\circ\text{C}$ did not show exothermic peaks for freezing. Independent melting point determination using a melting point apparatus did not show clear melting in the temperature range below 80°C either. Presumably, melting occurs only if a specific composition is achieved before 70°C . The TG curves shown in Fig. 1 clearly indicate this to be very sensitively dependent upon the experimental conditions.

The weight loss of about 2% upto 70°C in the TG curve recorded at the heating rate of $2 \text{ deg}\cdot\text{min}^{-1}$ using 51.3 mg of uranyl nitrate hexahydrate indicated that the composition corresponding to the constant weight plateau in the range $68\text{--}72^\circ\text{C}$ resulted from a mixture of the hydrates, $\text{H}[\text{UO}_2(\text{NO}_3)_3]\cdot 4\text{H}_2\text{O}$ and $[(\text{UO}_2\text{OH})_2(\text{H}_2\text{O})_4(\text{NO}_3)_2]\cdot 8\text{H}_2\text{O}$, formed [6] according to the reaction



The TG curve recorded with 51.3 mg of $\text{UO}_2(\text{NO}_3)_2\cdot 6\text{H}_2\text{O}$ at the heating rate of $2 \text{ deg}\cdot\text{min}^{-1}$ also showed a constant weight plateau in the range $35\text{--}40^\circ\text{C}$. The corresponding composition could be representative of an equilibrium mixture of $[\text{UO}_2(\text{NO}_3)_2(\text{H}_2\text{O})_2]\cdot 4\text{H}_2\text{O}$ and the products, $\text{H}[\text{UO}_2(\text{NO}_3)_3]\cdot 4\text{H}_2\text{O}$, $[\text{UO}_2(\text{OH})(\text{H}_2\text{O})_2\text{NO}_3]\cdot 4\text{H}_2\text{O}$ and H_2O resulting from the reaction:



The single crystal neutron diffraction studies on the structure of uranyl nitrate by Taylor and Mueller [12] have shown one of the nitrate groups to be bonded less strongly than the other to uranium. This could lead to preferential replacement of one of the nitrate groups with a hydroxyl group, during hydrolysis, and hence to the products suggested in Eqs (1) and (2).

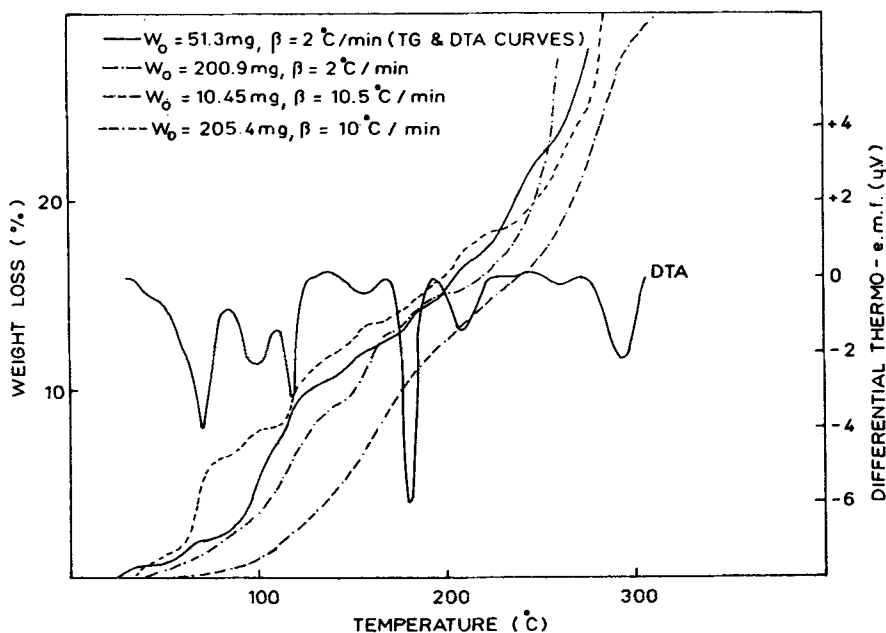


Fig. 1 Dehydration of uranyl nitrate hexahydrate in dynamic argon atmosphere

The decomposition of uranyl nitrate hexahydrate appeared to be a complicated process as evidenced by the presence of multiple evolution peaks for NO and NO₂ which indicated formation of several polymerised hydroxynitrates of uranium as intermediates during dehydration. These species decomposed at temperatures higher than the decomposition temperature of anhydrous uranyl nitrate and hence yielded multiple evolution peaks for oxides of nitrogen. Similar results attributed to polymerisation of uranyl nitrate during thermal decomposition have been reported by Addison *et al.* (loc. cit.). Higher heating rates and larger sample weights increased the presence of moisture in the sample environment during dehydration of the compound and this could lead to increased amounts of hydroxynitrates. This is supported by an increase in the ratio of peak

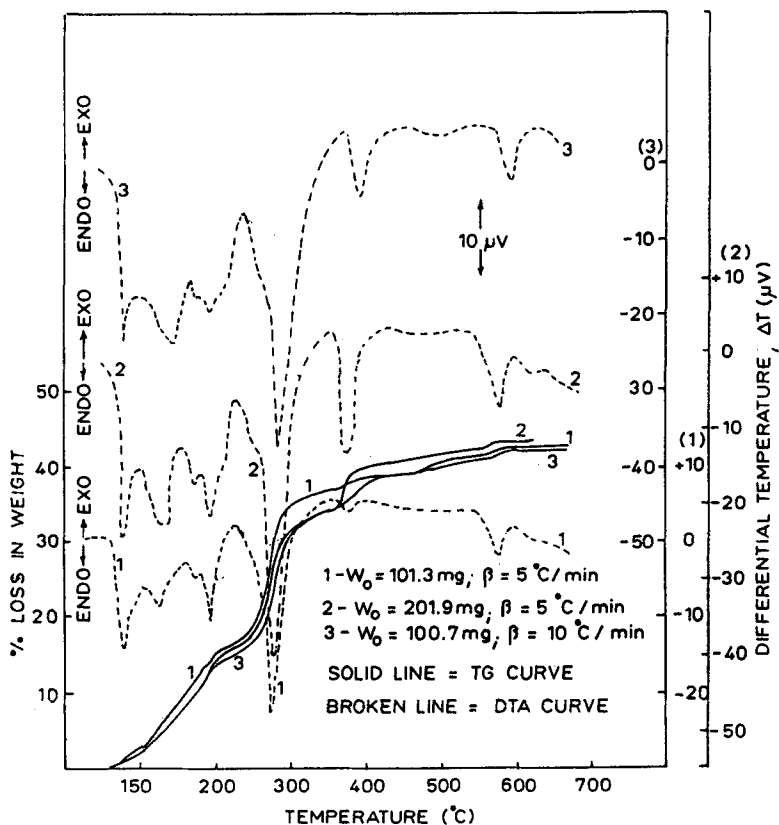


Fig. 2 Simultaneous TG-DTA of uranyl nitrate hexahydrate under different experimental conditions

height for NO evolution peak at about 375°C to that at about 275°C with increase in heating rate and sample weight (Fig. 3). The corresponding DTA peaks also showed a similar behaviour and the percentage weight loss upto the end of the first major NO evolution peak decreased with increase in sample size and heating rate (Fig. 2). At low heating rates and small sample weights the water vapour evolved during the dehydration reaction could be efficiently swept out from the sample environment before the attainment of higher temperatures. Hence the possibility of hydrolysis and polymerisation was minimal under these conditions. This decreased the amount and altered the stoichiometry of the hydroxynitrates.

Infrared spectra in nujol mull for the starting material as well as the decomposition residues prepared at various temperatures in the Netzsch Thermobalance showed peaks characteristic of nitrates [13] (750 cm^{-1} , 1030 cm^{-1} ,

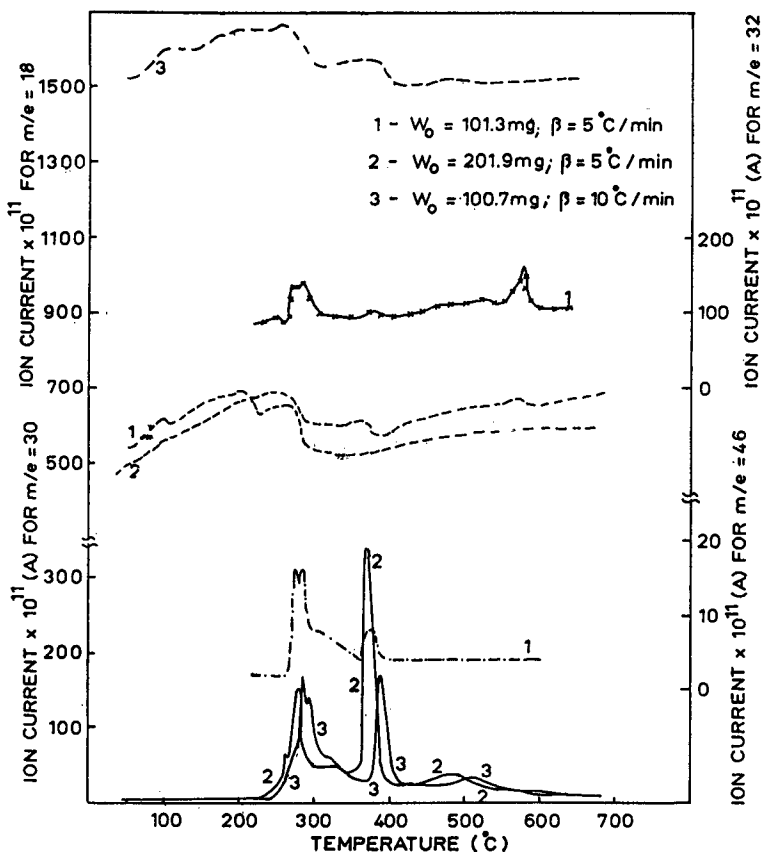


Fig. 3 EGA curves for the decomposition of uranyl nitrate hexahydrate (— NO, --- H₂O, - · - NO₂, - * - O₂)

1310 cm^{-1} and 1550 cm^{-1}) even in samples heated upto 420 $^\circ\text{C}$ (Fig. 4), in general agreement with the conclusions drawn from TG-DTA-EGA studies.

Conclusions

The results of the present TG-DTA-EGA measurements conclusively prove that uranyl nitrate hexahydrate undergoes extensive hydrolysis during dehydration. Hydrolysis occurs even when the sample size is of the order of 10 mg and the sample container is a shallow platinum pan. The products of hydrolysis undergo polymerisation and at least one of them undergoes melting. The extent of hydrolysis and polymerisation depend on the experimental conditions of heating rate, sample size and nature of containment of the sample. Contrary to earlier

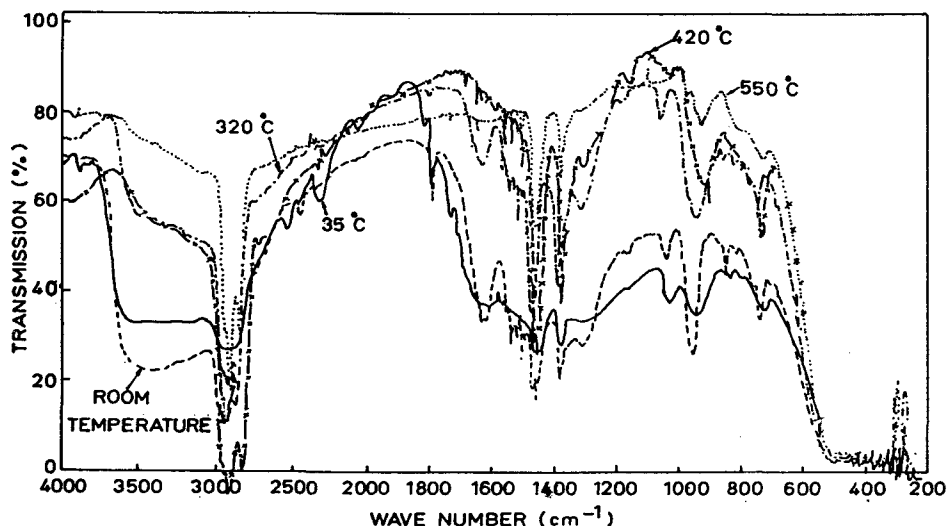


Fig. 4 Infrared spectra for uranyl nitrate hexahydrate heated upto various temperatures

claims, a constant weight plateau corresponding to anhydrous uranyl nitrate is not observed under any of the experimental conditions used in the present study. The dependence of the composition of hydroxynitrates of uranium, formed during dehydration, on experimental conditions affects the evolution pattern for oxides of nitrogen during their subsequent thermal decomposition. Further polymerisation of these hydroxynitrates during thermal decomposition, as observed for anhydrous uranyl nitrate, is also possible and the evolution of oxides of nitrogen is not completed before 500°C.

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Zusammenfassung — TG-DTA-EGA-Untersuchungen erwiesen, daß wasserfreies Uranylнитrat nicht durch die thermische Zersetzung von Uranylнитrathexahydrat erhalten werden kann. Während der Dehydratation stattfindende Hydrolyse und Polymerisation des Salzes führen zu Hydroxynitrat, die sich in mehreren Schritten unter Freisetzung von Stickoxiden und Wasser zersetzen. Das Ausmaß der Hydrolyse hing von Probengröße, Aufheizgeschwindigkeit und Art der Probenkontrolle ab. Große Proben zeigten bei der Zersetzung bei relativ hohen Aufheizgeschwindigkeiten die Freisetzung von Stickstoffmonoxid sogar oberhalb 500°C. Die Schlußfolgerungen wurden durch IR-Untersuchungen der bei verschiedenen Temperaturen erhaltenen Rückstände bestätigt.