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**Analysis of UO_3 Gel Microsphere
Decomposition Products by Mass Spectrometry**

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ANALYSIS OF UO_3 GEL MICROSPHERE DECOMPOSITION
PRODUCTS BY MASS SPECTROMETRY

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TABLE OF CONTENTS

	<u>Page</u>
ABSTRACT	1
INTRODUCTION	1
EXPERIMENTAL	2
RESULTS AND DISCUSSION	3
CONCLUSIONS	11
REFERENCES	13

ABSTRACT

UO₃ microspheres prepared by an internal gelation process were pyrolyzed, and the gaseous products were monitored by a time-of-flight mass spectrometer. The gel was heated from 25 to 800°C at various heating rates. Evolution profiles were made for each product by plotting ion current versus temperature. From the shape of the profile and the peak temperature of evolution, several hypotheses about the decomposition mechanism could be formulated. Estimates of the activity energy for the dissociation processes including the removal of water and ammonia from the spheres were made; the values were 9 kcal/mole and 20 kcal/mole, respectively.

INTRODUCTION

Uranium dioxide fuel particles produced by an internal gelation process¹ are being fabricated into light-water reactor fuel elements by the sphere-pac technique.² The U(VI) gel precipitation process for the production of UO₂ microspheres consists primarily of the precipitation of UO₃ hydrate by ammonia from a substoichiometric uranyl nitrate solution. This process utilizes the thermal degradation of hexamethylenetetramine (hexa) in solution to supply the necessary ammonia. Urea is used to protect the uranyl ions from premature precipitation and to increase the decomposition rate of hexa.¹ The reaction mixture is dispersed in droplets into a hot immiscible organic liquid, forming porous solid microspheres which are washed to remove ammonium nitrate, hexa, and urea. The chemical formula for the material at this stage is represented as UO₃ · (2 - x) H₂O · xNH₃ and is referred to as ammonium diuranate or simply ADU.

Infrared studies by Deane³ and later Zubova et al.⁴ indicate that the uranium(VI) oxide monohydrate does not contain water in the molecular form, but rather is represented as UO₂(OH)₂. In some ADU compounds, water and ammonia are also positioned about the central uranium atom and have the form UO₂(OH)₂ · xH₂O · yNH₃.

Four different compounds existing in the UO₂-H₂O-NH₃ system have been identified by Cordfunke⁵ and have the formulas shown below:

- (1) UO₃ · 2H₂O or UO₂(OH)₂ · H₂O
- (2) 3UO₃ · NH₃ · 5H₂O or UO₂(OH)₂ · 2/3 H₂O · 1/3 NH₃
- (3) 6UO₃ · 3NH₃ · 9H₂O or UO₂(OH)₂ · 1/2 H₂O · 1/2 NH₃

The products from the gel precipitation process probably have one or more of the above formulas.

After the gel spheres have been precipitated and washed, they are ready for reduction into dense UO_2 microspheres. It must be noted that a surfactant is added to the precipitating liquid to prevent the microspheres from sticking to one another or to the equipment columns. The gel spheres are washed with 0.5 M NH_4OH , dried, and usually calcined at 450°C to remove volatile materials. They are then sintered in a reducing atmosphere, and the dense UO_2 microspheres are formed. In this experiment, particles which had been air dried at room temperature and had not yet been calcined or reduced were pyrolyzed, and the gaseous products were studied by a time-of-flight mass spectrometer (TOFMS). From the identification of the evolved gases and the temperature of their appearance, information about the decomposition can be gained.

The products evolved upon thermal decomposition are given off at characteristic temperatures for a given heating rate. If a different rate is used, however, the peak temperature of evolution for a particular product is shifted. Faster heating rates cause the peak production of each gaseous product to occur at higher temperatures. It has been shown that the logarithm of the heating rate plotted against the inverse absolute peak temperature of evolution yields a straight line.⁶⁻⁷ The slope of such line is E_a/R , where E_a is the apparent activation energy for the decomposition of the substance into a product which has lost the gas of interest (i.e., H_2O , NH_3), and R is the gas constant, $2 \text{ cal} \cdot \text{deg}^{-1} \cdot \text{mole}^{-1}$.

In this experiment, ADU compounds were decomposed using a variety of heating rates, and the gaseous products were monitored over the entire temperature range using the TOFMS.

EXPERIMENTAL

Samples of UO_3 gel microspheres* weighing between 1 and 2 milligrams were placed in a quartz sample container (1 cm long, 1/4 cm diam). This container was inserted into a vacuum-tight inconel tube which could be

*70- μm particles supplied by Chemical Technology Division, ORNL.

attached directly to the flight tube of the TOFMS. This sample apparatus was placed in a horizontal tube furnace. The temperature of the furnace could be raised continuously and constantly by use of a setpoint voltage ramp and monitored with a type K (Chromel-Alumel) thermocouple with a digital readout. The mass spectrometer was a CVC Products, Inc., type MA-2 TOFMS, and the spectra obtained were recorded by use of a CSI-260 Digital Data System and a LA36-DE DECwriter. This data recording system printed the mass number and the ion current for each mass in the scans.

The gel samples were heated from 25 to 800°C, and the evolved gaseous decomposition products were monitored by the TOFMS. Scans of the mass spectrum were taken about once every 5 to 20 seconds. The TOFMS was operated in the "scan" mode, and the operating pressure was about 1.3×10^{-3} Pa. Heating rates of from 2°C/min to 27°C/min were used.

The evolution profiles for each m/e were obtained by plotting ion current versus temperature. The necessary corrections were made for interfering fragmentation patterns: the m/e 17 peak was corrected for H₂O contribution, and the m/e 28 peak was corrected for CO₂. The evolution profiles allowed the peak temperature of evolution to be identified. From the profiles, hypotheses concerning the nature of the hydrated ammonium uranates were formulated. Estimates of the activation energies for the removal of water and ammonia were also made.

RESULTS AND DISCUSSION

The gaseous products evolved from the pyrolysis of the gel microspheres and monitored by the TOFMS included m/e 12, 15, 16, 17, 18, 28, 32, and 44. Water (m/e 18) and ammonia (m/e 17) were the largest constituents of the evolved gas below 200°C. The gaseous species CO (m/e 28) and CO₂ (m/e 44) became appreciable at temperatures above 200°C.

For the slower heating rates, the H₂O evolution profile showed three distinct peaks (Fig. 1). These occurred around 100, 250, and 330°C. It has been suggested that the first peak is due to surface or occluded water in molecular form coordinated about the uranium atoms in the microspheres.⁸ The second peak probably corresponds to water from the dehydration of the hydroxyl groups; other sources of water include the combustion of trace

Fig. 1. Evolution profile for m/e 18 (H_2O) vs temperature

organics or possibly the self-reduction reaction as proposed by Price,⁹ in which U(VI) is reduced to U(IV) by retained ammonia, releasing water and nitrogen gas. In trials where a faster heating rate was used, the second two peaks were not distinct, but rather formed a broad band from about 200–300°C. However, the first peak was observed in all cases and appeared at increasingly higher temperatures as the heating rate was incremented (Fig. 2). The peak data for various heating rates, along with parameters used for estimating the activation energy, are recorded in Table 1. As can be seen in Fig. 3, the log of the heating rate versus the inverse absolute peak temperature yielded a straight line, and from its slope the activation energy for the removal of surface water is estimated as 9 kcal/mole. This may not only be the activation energy for the removal of water, but also may include the activation due to isomerization of a reactant. The assumptions made are that there is a real, single order of reaction and that the rate constant is completely described by the expression $Ae^{-E/RT}$. Since these conditions may not have been met, the activation energy for the removal of water may be somewhat less than 9 kcal/mole. However, the value is in fair agreement with values given for dehydration of outer sphere water from simple inorganic salts.¹⁰

Table 1. M/e 18 H₂O peak data

Heating rate, °C/min	Peak evolution temperature	Log, heating rate	1/T(K ⁻¹) x 10 ⁻³
6.2	89	0.792	2.762
8.3	100	0.919	2.681
14	116	1.146	2.571
19	124	1.279	2.519

The evolution profile for m/e 17, corrected by subtracting the H₂O contribution for each scan, showed one main peak occurring about 200–250°C. These peaks were much broader than the H₂O peaks. The temperature of peak evolution was again observed to increase with increasing heating rates, as seen in Fig. 4.

Fig. 2. First m/e 18 peak profiles at different heating rates

Fig. 3. Reciprocal of absolute temperature vs
log of heating rate for H_2O

Fig. 4. Profiles of m/e 17 (NH_3) at different heating rates

Data for the calculation of the energy of activation for the removal of ammonia are tabulated in Table 2. Fig. 5 illustrates the plot obtained, and the activation energy calculated is 20 kcal/mole.

Table 2. M/e 17 NH₃ peak data

Heating rate, °C/min	Peak evolution temperature	Log, heating rate	1/T(K ⁻¹) x 10 ³
2.4	206	0.380	2.088
7	228	0.845	1.996
14	248	1.146	1.919
27	269	1.431	1.845

The peak for m/e 44 appeared somewhere between 400 and 500°C for most of the trials. The profile was similar in all of the runs. The fact that CO₂ was evolved in fair quantity suggests that organic substances were being pyrolyzed, probably surfactant on the particles (0.1% by weight) or residual organic solvents. These two sources of organic products may also account for the m/e 28 peaks, which appeared at around 200 and 450°C. Another possibility for m/e 28 is nitrogen produced in the reduction reaction mentioned previously. However, no significant peaks at m/e 14, characteristic of nitrogen fragmentation, were observed.

Yet another possibility for the CO₂ origin is that it comes from urea. In his study of the urea process,¹¹ Hermans found that amorphous ammonia uranate precipitates contained up to 1% urea. Chemical analysis of his products yielded a carbon dioxide content of 4-5%. This reference also discussed the possibility of carbonate complexes; UO₂(CO₃)₃⁴⁻ and UO₂(CO₃)₂²⁻ can be formed under certain conditions from CO₂ produced by the hydrolysis of urea. Although the reaction

is very minimal (less than 1%) under the conditions of the KEMA process,¹² there is still a possibility of complex formation. CO₂ or CO₃²⁻ might be present as ligands in the precipitate, but to a lesser degree than H₂O or NH₃. However, there is no present experimental evidence for this aside

Fig. 5. Reciprocal of absolute temperature vs log of heating rate for NH_3

from the CO_2 content of Herman's amorphous product and the evolution of CO_2 during pyrolysis.

The m/e 32 peak occurred only sporadically around 500°C . This could be due to the release of oxygen when UO_3 is reduced. However, its unpredictable appearance suggests that oxygen produced by the reduction is probably also consumed in organic oxidations occurring simultaneously.

CONCLUSIONS

The evolution of water and ammonia upon heating urania gel microspheres occurred in an expected manner. Increasing the heating rate caused the evolution of these gaseous products to occur at higher temperatures. The relatively low values calculated for the activation energies are consistent with the present model of the ADU system. Water (1st water peak - Fig. 1) and ammonia are not present in the inner core of the molecule, but are weakly bound in the outer sphere surrounding the uranyl center. From this position they are easily removed upon heating.

The three peaks observed in the evolution profile of water illustrate that water is present in more than one form in ammonia uranates. Stuart and Whately¹³ showed that the 1610 cm^{-1} absorbance band, characteristic of the vibrational modes of coordinated water molecules, disappeared when $\text{UO}_3 \cdot 2\text{H}_2\text{O}$ was heated at 100°C for one hour. Heating to 300°C removed the 3350 cm^{-1} band (O-H stretch). These results indicate that the first peak in the evolution profile was due to loss of molecular water, while one of the other peaks occurring at higher temperature corresponded to the loss of water in hydroxyl form.

The facts that ammonia did not evolve until a higher temperature and is not completely removed upon hydrothermal treatment indicate that it is held by stronger bonds than molecular water.⁴ Stuart and Whately proposed that ammonia was present as NH_4^+ , but the current evidence is that it is in the form of NH_3 coordinated about the uranyl center.^{3-5,8-9} The activation energy calculated was greater for ammonia than water, which may also be indicative of the stronger uranyl-ammonia bonds.

The gel microspheres produced by the KEMA process contained more than UO_3 , NO_3 , and H_2O . The peaks produced in the mass spectra at m/e 28 and

44 were probably due to a combination of microsphere surfactant, urea, residual organic solvent used for preparation, and carbonate complexes formed from the hydrolysis of urea in the reaction mixture. During the final stages of microsphere production, these volatiles are removed by calcination, sintering, and reduction.

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