Thermochimica Acta, 155 (1989) 283–295
Elsevier Science Publishers B.V., Amsterdam – Printed in The Netherlands

PROPERTIES AND THERMAL DECOMPOSITION OF THE DOUBLE SALTS OF URANYL NITRATE–AMMONIUM NITRATE

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(Received 4 April 1989)

ABSTRACT

The formation of ammonium nitrate–uranyl nitrate double salts has important effects on the thermal denitration process for the preparation of UO_3, and on the physical properties of the resulting product. Analyses have been performed, and properties and decomposition behavior determined for three double salts: $NH_4UO_2(NO_3)_3$, $(NH_4)_2UO_2(NO_3)_4$ and $(NH_4)_2UO_2(NO_3)_4 \cdot 2H_2O$. The trinitrate salt decomposes without melting at 270–300 ° C to give a γ-UO_3 powder of average size approximately 3 μm, with good ceramic properties for fabrication into UO_2 nuclear fuel pellets. The tetranitrate dihydrate melts at 48 ° C; it also dehydrates to the anhydrous salt. The anhydrous tetranitrate decomposes exothermically without melting at 170–270 ° C, by losing one mole of ammonium nitrate to form the trinitrate salt.

INTRODUCTION

Thermal denitration is used to prepare uranium oxides on a large scale as one process step for conversion of uranyl nitrate $[UO_2(NO_3)_2]$ solutions to UO_3. The UO_3 can then be reduced to UO_2 for eventual conversion to uranium metal or UF_6 [1]. Excess HNO_3 in the $UO_2(NO_3)_2$ solution can be neutralized with NH_4OH solution or NH_3 to reduce corrosion. This has been observed to cause precipitation of $NH_4UO_2(NO_3)_3$ crystals [2].

Uranium dioxide powder is also a feed for the fabrication of fuel pellets for nuclear reactors, but in the past, UO_2 derived via thermal denitration of $UO_2(NO_3)_2$ has not yielded acceptable pellets. It has recently been discovered that the ceramic properties of UO_2 for fabrication of nuclear fuel pellets can be greatly improved by the addition of NH_4NO_3 to the $UO_2(NO_3)_2$ feed solution prior to denitration [3]. The formation of double salts of NH_4NO_3–$UO_2(NO_3)_2$ is important to these results. The present work investigates the properties and pyrolysis of these double salts. Measurements made included chemical analyses, X-ray and optical data, differential thermal analyses, thermogravimetric analyses and effluent gas analyses.

0040-6031/89/$03.50

Three double salts are known for the $UO_2(NO_3)_2$–NH_4NO_3–H_2O system, but relatively little information about these salts has been reported in the literature. Colani [4] has reported that $(NH_4)_2UO_2(NO_3)_4 \cdot 2H_2O$ is the only stable salt at equilibrium. Staritzky and Truitt [5] have observed $(NH_4)_2UO_2(NO_3)_4$ and $NH_4UO_2(NO_3)_3$ under nonequilibrium conditions. The trinitrate salt is the stable form in acidic solutions [6]. Optical data on these compounds have been reported [5,7], including refractive index, optic angle and color. Complex formation of 1 : 1 and 2 : 1 NH_4^+/UO_2^{2+} in nitrate solution has also been described [8].

A double salt of Pu(IV) nitrate and ammonium nitrate [$(NH_4)_2Pu(NO_3)_6 \cdot 2H_2O$] and a possible double salt of Pu(VI) nitrate and ammonium nitrate have been reported [9]. This suggests the possibility of mixed double salts of uranium, plutonium and ammonium nitrates, which may have application to the co-denitration of uranium and plutonium nitrates in the fabrication of mixed oxide fuels for fast breeder reactors.

PREPARATION AND PHYSICAL PROPERTIES OF SAMPLES

Small amounts of the double salts were prepared for characterization from a solution consisting of 70 wt.% $UO_2(NO_3)_2 \cdot 6H_2O$, 20 wt.% NH_4NO_3 and 10 wt.% water, for a mole ratio NH_4^+/UO_2^{2+} of 1.8 : 1.

Diammonium uranyl tetranitrate dihydrate was prepared by slowly evaporating the above solution at room temperature. Selective formation of the dihydrate was favored by dissolving a small quantity of UO_3 to decrease the hydrolytic acidity of the solution. When this was not done, $NH_4UO_2(NO_3)_3$ also crystallized. Ammonium uranyl trinitrate was selectively salted out of a solution of the above composition by the addition of concentrated HNO_3. Diammonium uranyl tetranitrate was obtained by dehydrating the dihydrate in a vacuum desiccator at room temperature.

Crystallization from various other solutions yielded $UO_2(NO_3)_2 \cdot 6H_2O$, NH_4NO_3, and mixtures of the double salts. Solutions containing > 22% NH_4NO_3 at first yielded long, strained crystals of ammonium nitrate, and then formed a double salt.

Chemical analyses of the double salts prepared by the above procedures are given in Table 1, along with the calculated values for the stoichiometric compositions. Also given are densities as determined by pycnometric displacement of xylene. The literature gives a density for the dihydrate only [7], with a value of 2.777 g ml^{-1} as compared with our determined value of 2.79 g ml^{-1}.

Morphological properties were not investigated because the crystals had poorly developed anhedral forms. Refractive indices and color agreed closely with reported data [5]. Reported crystal morphologies are given in Table 2. All three compounds are pleochroic. This property is most pronounced in

TABLE 1

Analysis of ammonium uranyl nitrates

	Composition (wt.%)	
	By analysis	Calculated
$(NH_4)_2UO_2(NO_3)_4 \cdot 2H_2O$		
U	40.34	40.35
NO_3^-	40.3	42.03
NH_3	5.70	5.76
H_2O	6.05	6.10
Density (g ml^{-1})	2.79	
$(NH_4)_2UO_2(NO_3)_4$		
U	42.76	42.96
NO_3^-	44.2	44.77
NH_3	6.18	6.14
Density (g ml^{-1})	2.84	
$NH_4UO_2(NO_3)_3$		
U	48.80	50.22
NO_3^-	39.0	39.23
NH_3	3.49	3.58
Density (g ml^{-1})	3.10	
$NH_4UO_2(NO_3)_3$ [a]		
U	49.41	
NO_3^-	40.54	
NH_3	4.2	

[a] Prepared in a large batch at 190/240 °C.

the trinitrate, which exhibits yellow-green and pale yellow. The anhydrous tetranitrate is faintly greenish-yellow in one direction and yellow in the other two, while the hydrate is pale yellow in two directions and colorless in the third.

X-ray diffraction data were obtained with a Norelco spectrometer, using Cu $K\alpha$ radiation and a scanning speed of 0.5° min^{-1}. The interplanar spacings and their relative intensities, previously unreported, are given in Table 3.

Larger amounts of $NH_4UO_2(NO_3)_3$ were prepared by evaporating solutions with $UO_2(NO_3)_2$ and NH_4NO_3 (mole ratio UO_2^{2+}: NH_4^+, 1:2) at

TABLE 2

Reported crystal morphologies

Compound	Morphology	Reference
$NH_4UO_2(NO_3)_3$	Rhombohedral	Steinmetz, in ref. 7
$(NH_4)_2UO_2(NO_3)_4$	Monoclinic	Ref. 5
$(NH_4)_2UO_2(NO_3)_4 \cdot 2H_2O$	Monoclinic	Nichols, in ref. 7

TABLE 3

X-ray diffraction data

$NH_4UO_2(NO_3)_3$		$(NH_4)_2UO_2(NO_3)_4$		$(NH_4)_2UO_2(NO_3)_4 \cdot 2H_2O$	
d(Å)	100 I/I_0	d(Å)	100 I/I_0	d(Å)	100 I/I_0
6.18	100	6.64	90	6.77	60
4.70	55	6.13	100	6.51	80
4.09	70	5.20	5	6.08	60
3.77	20	4.93	40	5.71	90
3.74	30	4.69	10	4.52	30
3.15	25	4.17	90	4.36	30
3.08	20	4.08	5	3.86	20
2.92	30	3.79	30	3.76	25
2.711	25	3.63	15	3.71	10
2.616	10	3.58	10	3.58	5
2.577	25	3.32	20	3.50	100
2.344	35	3.14	20	3.39	10
2.270	15	2.98	5	3.30	20
2.264	10	2.807	15	3.25	20
2.192	20	2.622	10	3.04	20
2.040	15	2.571	15	2.91	20
1.985	10	2.461	15	2.795	20
1.877	15	2.423	10	2.715	10
1.841	10	2.343	5	2.634	5
1.829	10	2.320	5	2.546	10
		2.199	10	2.519	15
		2.171	5	2.488	10
		2.085	10	2.433	10
		2.042	10	2.403	25
		2.001	5	2.237	20
		1.977	5	2.186	10
		1.952	5	2.171	10
		1.881	5	2.146	5
				2.122	5
				2.025	5
				1.960	5
				1.905	10
				1.885	10
				1.753	10
				1.737	30
				1.706	5
				1.683	10

190 ° C, and then heating at 240 ° C. This material was used to prepare UO_3 for subsequent use in pellet fabrication tests, after reduction to UO_2 with hydrogen [3]. Analysis of the product (Table 1) clearly shows it to be the trinitrate. Based on the weight loss at 190 ° C, it is believed that under these preparation conditions significant amounts of the tetranitrate form as an

intermediate. Batch evaporations at 190 °C gave a product approximating the trinitrate from a 1 : 1 $NH_4^+ : UO_2^{2+}$ nitrate solution, and approximating the tetranitrate from a 2 : 1 $NH_4^+ : UO_2^{2+}$ nitrate solution.

THERMAL DECOMPOSITION OF THE DOUBLE SALTS

Direct visual observation showed that both of the anhydrous double salts decompose from the solid state without melting, in the temperature range 150–300 °C. This contrasts strongly with the two pure components, $UO_2(NO_3)_2$ and NH_4NO_3, both of which melt prior to decomposition. This indicates strong crystal bonding for the double salts. The thermal decomposition of $UO_2(NO_3)_2$ to UO_3 leads to a sticky, mastic intermediate state (the "dough stage") which creates problems in physical handling and yields a lumpy product of low surface area. The anhydrous double salts, however, decompose without melting to yield a free-flowing UO_3 of relatively high surface area. The decomposition itself is rather quiescent; the anhydrous double salts can be formed into mounds at 190 °C and then decomposed to UO_3 without loss of the stir-marks or mound shapes. $(NH_4)_2UO_2(NO_3)_4 \cdot 2H_2O$ melts at 48 °C, and then dehydrates at a somewhat higher temperature to yield the anhydrous tetranitrate. At a low relative humidity, dehydration can occur below the melting point.

The UO_3 products derived from ammonium uranyl nitrates had BET surface areas of 5–7 $m^2\ g^{-1}$, as compared with 0.2–3 $m^2\ g^{-1}$ for UO_3 prepared from $UO_2(NO_3)_2 \cdot 6H_2O$ (UNH). UO_3 product which is easily dispersable to particles of which > 99% are smaller than 12 μm in diameter (with average particle diameters of 2.5–3.6 μm) can be obtained by decomposition of the double salts [3]. Fabrication of UO_2 pellets from this powder using a sintering temperature of 1450 °C yielded pellets of 91–92% of theoretical density with good microstructures; UO_3 from $UO_2(NO_3)_2$ solutions without NH_4NO_3 gave pellets of about 70% of theoretical density with poor microstructure for the same test conditions [3].

Thermogravimetric analysis

Thermogravimetric (TG) analysis was performed on all three double salts and on the two single salts. Figure 1 shows the decomposition curve for $(NH_4)_2UO_2(NO_3)_4 \cdot 2H_2O$, with the calculated weights of the intermediate compositions. It is clear that thermal decomposition proceeds in three distinct steps.

Dehydration

$$(NH_4)_2UO_2(NO_3)_4 \cdot 2H_2O \xrightarrow{\sim 40\,^\circ C} (NH_4)_2UO_2(NO_3)_4 + 2H_2O \qquad (1)$$

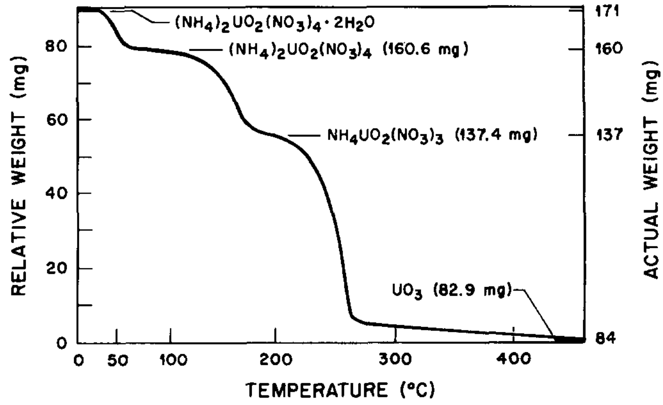

Fig. 1. Thermogravimetric analysis of $(NH_4)_2UO_2(NO_3)_4 \cdot 2H_2O$. Initial sample weight, 171 mg.

Loss of 1 mole NH_4NO_3

$$(NH_4)_2UO_2(NO_3)_4 \xrightarrow{\sim 170\,^\circ C} NH_4UO_2(NO_3)_3 + N_2O + 2H_2O \qquad (2)$$

Conversion to UO_3

$$NH_4UO_2(NO_3)_3 \xrightarrow{\sim 270\,^\circ C} UO_3 + (N_2O_5) + N_2O + 2H_2O \qquad (3)$$

When starting with $(NH_4)_2UO_2(NO_3)_4$, only steps (2) and (3) are observed; and when starting with $NH_4UO_2(NO_3)_3$, only step (3) occurs. For $UO_2(NO_3)_2 \cdot 6H_2O$, several steps are observed, corresponding roughly to dehydration to the tri-, di- and monohydrates, followed by loss of both water and nitrate to form a product roughly corresponding to a subnitrate, $UO_2(OH)_{0.5}(NO_3)_{1.5}$, which converts to UO_3 over the same temperature range as for step (3) above. The decomposition products for reactions (2) and (3) are inferred on the basis that NH_4NO_3 decomposes under controlled conditions to H_2O and N_2O (a standard method for the preparation of nitrous oxide).

$$NH_4NO_3 \overset{\Delta}{\rightarrow} N_2O + 2H_2O + 8.6\ \text{kcal} \qquad (4)$$

The final products were verified as being UO_3 by visual examination (orange color) and X-ray diffraction analysis. Interestingly, directly crystallized $NH_4UO_2(NO_3)_3$ yielded γ-UO_3 (the product of UNH decomposition also), while the trinitrate resulting from pyrolysis of the tetranitrate yielded an X-ray amorphous UO_3. The latter could be partially crystallized by further heating, above 500 °C, to the point where some oxygen loss might be expected. The diffraction pattern of this product gave only a few lines, which could be either α-UO_3 or the $UO_{2.92}$ phase [10]. The latter is the more likely, in view of the oxygen loss. For all of the UO_3 denitration products, heating to 560 °C in an inert atmosphere caused conversion to U_3O_8. Loss of oxygen at this temperature was verified by effluent gas analysis.

Differential thermal analysis

Differential thermal analysis (DTA) curves for all three double salts are shown in Fig. 2. After having established that the relatively sharp endotherm at ~ 50 °C results from melting of the dihydrate, the other three thermal effects were shown to correspond to the three reactions identified previously by TG analysis, but with higher reaction temperatures (Table 4). An explanation of these temperature shifts is based on the different conditions used for the DTA and TG runs. The DTA runs were performed in restricted sample wells, so that decomposition gases tended to be retained. The TG runs were performed in a shallow layer in flowing helium, so that decomposition gases were swept away as quickly as they were formed.

Thermal decomposition reactions can be strongly affected by the heating rate or the concentrations of decomposition products in the ambient atmosphere. Both the temperature at which the reaction occurs and the tempera-

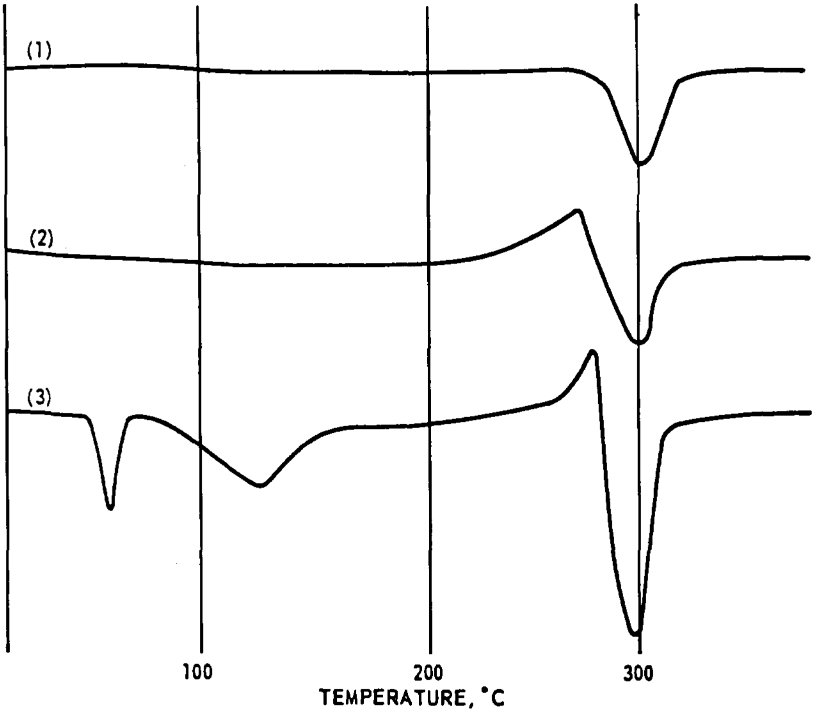

Fig. 2. Differential thermal analysis of (1) $NH_4UO_2(NO_3)_3$, (2) $(NH_4)_2UO_2(NO_3)_4$ and (3) $(NH_4)_2UO_2(NO_3)_4 \cdot 2H_2O$: upward deflection, exothermic effect; downward deflection, endothermic effect.

TABLE 4

Thermal decomposition reactions

Reaction	Temperature of maximum rate (° C)		Heat of reaction
	TG	DTA	
(1) Dehydration	40	120	Endothermic
(2) Loss of NH_4NO_3	170	270	Exothermic
(3) Conversion to UO_3	270	300	Endothermic

ture range over which the reaction is accomplished [11] can be altered by the decomposition product pressures. For example, dehydration occurs earlier and proceeds faster in TG than in DTA runs because the water vapor is swept away as fast as it is produced. In DTA, released water vapor is retained and can cause rehydration unless the temperature is high enough for the decomposition pressure to exceed the ambient vapor pressure. As noted previously, the dihydrate can be slowly dehydrated at room temperature in a vacuum desiccator; also, the anhydrous tetranitrate salt will hydrate at room temperature under humid conditions. Similar considerations of ambient decomposition product concentrations apply to reactions (2) and (3).

The same effect was noted in the controlled decomposition of NH_4NO_3 in a thermobalance (TG): with the products swept away, reaction occurred just above the melting point, at about 190 ° C, while DTA in a restricted volume delayed reaction to about 250 ° C. The DTA scan (Fig. 3) had sharp endotherms corresponding to the phase transitions of NH_4NO_3.

$$\text{alpha} \overset{32\,^\circ\text{C}}{\rightleftharpoons} \text{beta} \overset{84\,^\circ\text{C}}{\rightleftharpoons} \text{rhombohedral} \overset{125\,^\circ\text{C}}{\rightleftharpoons} \text{cubic}$$

In some cases the phase transition was delayed by time requirements for nucleation. The melting point (169 ° C) was observed as a sharp endotherm. The decomposition itself was also endothermic rather than exothermic, as expected from reaction (4). This result will be discussed later.

The two low-temperature endotherms of the dihydrate were at first thought to represent loss of water one mole at a time (under restricted atmospheric conditions), but visual observation showed that melting occurred and was responsible for the first endotherm. This was verified on DTA by cooling curves: cooling immediately after the first endotherm resulted in an exotherm owing to freezing, while cooling after the second endotherm, allowing time for the water vapor to escape, showed no thermal effects since the solid, anhydrous product could neither hydrate nor freeze. Conventional measurements in a closed capillary tube showed the melting point to be 48 ° C.

The exothermic loss of the first mole of NH_4NO_3 from the tetranitrate corresponds to the expected decomposition products (reactions (2) and (4)).

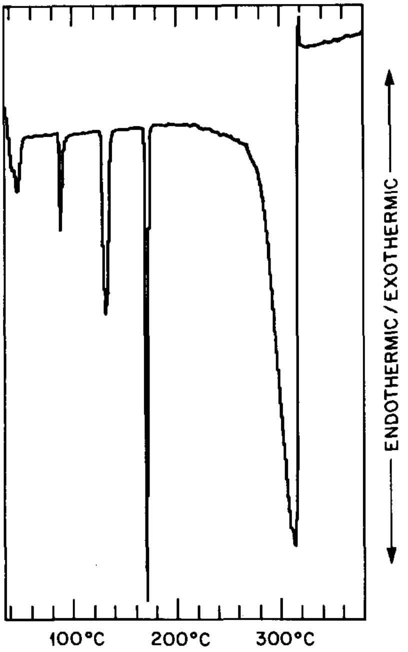

Fig. 3. Differential thermal analysis of NH_4NO_3.

Normally, thermal decompositions are endothermic, requiring heat input as well as elevated temperature, but reaction (4) is exothermic.

Effluent gas analysis

Effluent gas analysis (EGA) was done by mass spectrometry. The nature of the measurement allowed only semiquantitative interpretation. Excitation was required to produce positively charged ions for detection. Samples were reacted under vacuum, giving atmospheric conditions approaching those of the TG runs. Results are summarized in Table 5. Ammonium nitrate and a dehydrated $UO_2(NO_3)_2$ were also run; the $UO_2(NO_3)_2$ probably contained some hydroxyl water, present as the basic nitrate, $UO_2(OH)_{0.5}(NO_3)_{1.5}$.

For each sample, the major decomposition occurred at about the previously noted TG temperatures. For $UO_2(NO_3)_2$, the major products were oxidized species, as expected, with minor amounts of H_2O and reduced species. For NH_4NO_3, the N_2O appeared as a minor component, while NH_x species were quite strong and H_2O appeared as a major component. These results are not in agreement with reaction (4), and will be discussed later.

The trinitrate reacted in a single step, yielding products at a distinctive temperature which were similar, but not equivalent, to the sum of those produced from $UO_2(NO_3)_2$ and NH_4NO_3. The tetranitrate decomposed in two steps, the first step giving products corresponding to the loss of

TABLE 5

Effluent gas analysis of decomposition products

Analytical results		Temperature of maximum rate (°C)				
Mass no.	Species	$UO_2(NO_3)_2$ 320	NH_4NO_3 185	$NH_4UO_2(NO_3)_3$ 280	$(NH_4)_2UO_2(NO_3)_4$	
					185	290
14	N^+	m[a]	t[b]	M[c]	m	M
15	NH^+		M	m	M	M
16	NH_2^+	m	M	m	M	m
17	NH_3^+		M	m	M	
18	H_2O^+	m	M	M	m	M
28	N_2^+	m		m		m
30	NO^+	M		M		M
32	O_2^+	M		M		M
44	N_2O^+		m	M	m	M
46	NO_2^+	M		M		M

[a] m = minor component.

[b] t = trace component.

[c] M = major component.

NH_4NO_3 by reaction (4), the second step corresponding to decomposition of the trinitrate.

Batch thermal decompositions were also carried out in closed systems, collecting the evolved gases over water. For $UO_2(NO_3)_2$, very little insoluble gas (oxygen) was formed; all of the nitrate appeared as nitric and nitrous acids. With the mixed salts containing NH_4NO_3, the insoluble gases collected were approximately 25% N_2O, 25% O_2 and 50% N_2. The total amount of N_2O and N_2 collected corresponded to the nitrogen content of the contained NH_4NO_3. The presence of N_2 and O_2 suggests that a large fraction of the NH_4NO_3 component must have decomposed by a pathway other than reaction (4).

THERMAL DECOMPOSITION OF AMMONIUM NITRATE

In addition to decomposition by reaction (4), NH_4NO_3 can also decompose to yield N_2 and O_2.

$$NH_4NO_3 \rightarrow 2H_2O + N_2 + 0.5O_2 + 28.2 \text{ kcal} \quad (5)$$

This reaction is strongly exothermic and occurs when NH_4NO_3 explodes. Dissociation

$$NH_4NO_3 \rightarrow HNO_3 + NH_3 - 34.9 \text{ kcal} \quad (6)$$

has been proposed as playing a role in the decomposition mechanism [12,13], and also in the chloride-catalyzed decomposition [14]. Rozman [13] has proposed a mechanism involving the intermediate formation of nitrosamine, NH_2NO, to explain the formation of N_2 and O_2 at temperatures below 200 °C, but EGA of NH_4NO_3 showed neither nitrogen nor oxygen. The thermal decomposition of NH_4NO_3 is known to be catalyzed by chloride ion [15] and traces may have been present. The mechanism proposed for the chloride-catalyzed reaction involves both nitrosamine and chloramine, which yield N_2 as a product [14]. Multi-valenced metals also act as decomposition catalysts [16] and uranium may well function in this capacity. The joint presence of chloride and multi-valenced metals has a pronounced synergistic effect [17] which would serve to magnify the individual catalytic possibilities.

Since EGA of NH_4NO_3 decomposition showed only a minor amount of N_2O and major amounts of NH_x species, under our conditions reaction (4) does not appear to be the dominant decomposition pathway. Reaction (5) could account directly for the presence of O_2 and N_2, while reaction (6) could account directly for NH_x species and could also serve as a precursor to other reactions. Since reaction (5) is exothermic while reaction (6) is endothermic, DTA of NH_4NO_3 (Fig. 3) clearly supports the occurrence of reaction (6). Further reaction could occur from the products of reaction (6), but his could occur downstream from the thermal sensing area. Keenan [15], using totally different equipment, noted a very weak, broad exotherm for NH_4NO_3 decomposition but observed sharp, large exotherms when a chloride catalyst was present. Thus, in thermal analyses of NH_4NO_3 there are a number of factors which could alter the decomposition pathway, or confuse the interpretation of the data, or both.

Our observations are consistent with the following explanation. The NH_4NO_3 decomposition, being endothermic, must have involved a significant amount of reaction (6); reactions (4) and (5) may also have occurred, but to such a degree that the net effect was still endothermic. By measuring the areas under the peaks for decomposition and melting and by using the latter as a standard ($\Delta H_{\text{fusion}} = 1.3$ kcal mol^{-1}), we computed a heat of reaction of 10.4 kcal, which is equivalent to 44% dissociation by reaction (6) and 56% decomposition by reaction (4). This also correlates approximately with the gaseous species observed: NH_x and H_2O as major products, and N_2O as a minor product. The N^+ species observed is not from N_2; it is part of the fragmentation pattern of NH_3 (as are NH^+ and NH_2^+). There may also have been an "overlapping" of reactions, since the DTA traces of NH_4NO_3 decomposition were not completely "clean". The small exothermic blip at the end of decomposition (Fig. 3) suggests that after reaction (6) has run its course, reaction (4) or (5) continues to occur to a slight degree.

The first decomposition step of $(NH_4)_2UO_2(NO_3)_4$, corresponding to loss of NH_4NO_3, yields decomposition products similar to those obtained with NH_4NO_3, but the net thermal effect is exothermic. This suggests a simultaneous occurrence of reactions (5) and (6) to achieve the thermal effect observed, with a small amount of reaction (4) to produce the minor quantity of N_2O.

The final step in the decomposition of $NH_4UO_2(NO_3)_3$ is endothermic, but it yields major amounts of N_2O. This can be interpreted on the basis that the NH_4NO_3 portion of this compound decomposes as shown in reaction (4), while the $UO_2(NO_3)_2$ portion decomposes in a manner characteristic of that compound. The net endothermic heat effect results from the large negative heat of reaction of the latter reaction, which overrides the relatively small positive heat of reaction from reaction (4). The major role of reaction (4) in the NH_4NO_3 portion of the decomposition at this step could be caused by the higher reaction temperature or the catalytic influence of uranium. Detailed examination of these reaction mechanisms should be interesting.

ACKNOWLEDGEMENTS

This report includes unpublished data from work by K.J. Notz at the National Lead Company of Ohio, Fernald, OH. Effluent gas analyses were done at the Oak Ridge National Laboratory, Oak Ridge, TN, by D.A. Lee.

The research was sponsored by the Office of Facilities, Fuel Cycle, and Test Programs, U.S. Department of Energy, under contract DE-AC05-84OR21400, with Martin Marietta Energy Systems, Inc. The Oak Ridge National Laboratory is operated by Martin Marietta Energy Systems, Inc., for the U.S. Department of Energy.

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