THE THERMOLYSIS OF THE RARE EARTH AND OTHER METAL NITRATES

by

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In a recent study involving the determination of the solubilities of some rare earth and other metal nitrates in organic solvents^{1,2}, it was found that little was known concerning the thermal decomposition of these nitrates to their corresponding oxides. This information was desired because the organic solvent solutions of the metallic nitrates were evaporated and the resulting residues ignited and weighed as the metal oxides.

Previous investigations on the thermal decomposition of the hydrated rare earth nitrates were concerned mainly with the composition of the intermediate products formed and not the temperature limits for the appearance of the oxide levels^{3,4,5}. As a result of this incomplete information, the hydrated nitrates of scandium, yttrium, uranium(VI), thorium, zirconium, lanthanum, cerium(III), praseodymium, neodymium and samarium were pyrolyzed on the thermobalance.

EXPERIMENTAL

Chemicals

The sources of the yttrium and rare earth compounds have been previously described⁶. Scandium oxide of 99.8% purity was obtained from A. D. Mackay & Co., New York, N.Y. Uranium(VI) nitrate hexahydrate, reagent grade, was obtained from Merck & Co., Rahway, N. J. Zirconyl nitrate pentahydrate, C.p., was obtained from the E. H. Sargent and Co., Chicago, Ill. Thorium nitrate tetrahydrate was obtained from the Lindsay Chemical Co., West Chicago, Ill. All other chemicals were of analytical reagent grade.

Preparation of the hydrated metal nitrates

For those metals not obtained in the form of the nitrates, the hydrated nitrates were prepared. The metal oxides were dissolved in a minimum volume of 6N HNO₃ and after evaporating to a small volume, were allowed to crystallize. The resulting crystals of the metal nitrates were then pyrolyzed on the thermobalance.

Thermobalance

The construction and operation of the thermobalance has previously been described⁷. Sample sizes ranged from 100-200 mg. The heating rate for all samples was 4.5°/min.

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DISCUSSION

Rarc earth nitrates

All of the rare earth nitrate hexahydrates decomposed in the same general manner except cerium(III). The water of hydration began to come off in the temperature range 30 to 50° with the formation of intermediate hydrates of varying stabilities until a horizontal was reached containing the anhydrous metal nitrate. The anhydrous metal nitrates then decomposed to give oxynitrates of the general formula, $MONO_3$, which subsequently decomposed to give the corresponding metal oxides. The thermolysis curves are shown in Fig. 1 with the minimum temperature limits for the oxide levels given in Table I.



Lanthanum nitrate hexahydrate. The hexahydrate began to lose water of hydration at 50° and gave inflections in the thermolysis curve at the pentahydrate and dihydrate compositions. However, no horizontals were observed because of the heating rate employed. A horizontal corresponding to the monohydrate began at 170° which lost water to form the anhydrous salt, $La(NO_3)_3$, at 240°. The anhydrous salt began to lose oxides of nitrogen at 420° resulting in a horizontal at 515° of the oxynitrate, LaONO₃. This began to decompose at 575° and resulted in the formation of La_2O_3 at 780°. The thermolysis of this compound shows that the anhydrous lanthanum nitrate can be prepared by heating the hydrated salt.

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Metal nitrate	Uxide	Temperature °C	
Lanthanum	La ₂ O ₂	780	
Cerium(III)	CeÔz	450	
Praseodymium	Pr _a O ₁₁	505	
Neodymium	Nd.O.	830	
Samarium	Sm ₂ O ₃	750	
Scandium	Sc,Ô,	510	
Yttrium	Y.O.	480	
Uranium	U,O,	5.50	
Thorium	ThO,	480	
Zirconium	ZrO	575	

TABLE I

MINIMUM	OXIDE	TEMPERATURE	LIMITS	FOR	THE	METAL.	NITRATES
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Heating rate of 4.5°/min

Cerium(III) nitrate hexahydrate. The thermolysis pattern of cerium(III) nitrate was different from those of the other rare earth metal nitrates. Instead, the decomposition pattern was similar to that of thorium nitrate. No intermediate hydrates were detected nor was $CeONO_3$ found in the thermolysis curve. The hexahydrate was stable up to 80° where it gradually lost water and finally oxides of nitrogen to give the CeO_2 horizontal beginning at 450° .

Prascodymium nitrate hexahydrate. The hexahydrate began to lose water at 50° but no well defined horizontals of intermediate hydrates were found. The loss of water resulted in a horizontal which began at 300° for the anhydrous Pr(NO₃)₃. The anhydrous nitrate began to lose oxides of nitrogen at 375° and gave a break in the curve at 470 to 480° corresponding to PrONO₃. The oxide, Pr₆O₁₁, appeared at 505°. Neodymium nitrate hexahydrate. The hexahydrate began to lose water at room temperature. No intermediate hydrates were detected. The anhydrous $Nd(NO_a)_a$ was stable from 290 to 380°. This is perhaps the first time that the anhydrous nitrate was prepared by thermal decomposition of the hydrated salt at atmospheric pressure. SELWOOD⁹ previously prepared the anhydrous nitrate by heating the hexahydrate under several mm of Hg pressure. The anhydrous nitrate began to lose oxides of nitrogen at 380° and gave a break in the curve at about 475° which corresponded to the oxynitrate, $NdONO_3$. No well defined horizontal was obtained due perhaps to the excessive heating rate employed. A horizontal corresponding to the oxide, $Nd_{2}O_{2}$, was obtained beginning at 830°. This was the highest minimum oxide temperature obtained from all of the compounds studied. This is not surprising however because DUVAL⁸ found that the oxide level in neodymium oxalate did not appear until 813°.

Samarium nitrate hexahydrate. The hexahydrate was stable to about 50° where it began to lose water. No intermediate hydrate horizontals were detected nor was there a horizontal corresponding to the anhydrous $Sm(NO_3)_3$. An oxynitrate, $SmONO_3$, did appear in a horizontal in the temperature range of 450 to 490°. The oxide horizontal of Sm_2O_3 appeared at 750°.

Yttrium and scandium nitrates. The thermolysis curves are shown in Fig. 2 with the temperature limits for the oxide levels given in Table I. Yttrium nitrate hexahydrate began to lose water at room temperature but intermediate hydrate horizontals were not detected. A horizontal corresponding to the anhydrous $Y(NO_3)_3$ was not detected

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either. A short horizontal at 440 to 475° corresponding to the oxynitrate, $YONO_3$, was found. The oxide horizontal began at 660°. In many respects the thermolysis curve of this compound was similar to that of samarium nitrate.

Scandium nitrate hexahydrate decomposed to give horizontals which did not correspond to the anhydrous $Sc(NO_3)_3$ or the oxynitrate, $ScONO_3$. The horizontals obtained did not correspond to any stoichiometric compounds and were probably mixtures. The oxide horizontal appeared at 510°.



Thorium, zirconyl and uranium(VI) nitrates

The thermolysis curves are shown in Fig. 2 with the minimum oxide temperatures given in Table I. The thermolysis curves of thorium and zirconyl nitrates were similar in appearance. In neither case was a horizontal obtained which corresponded to the anhydrous metal nitrates. The ThO₂ horizontal began at 480° while that of ZrO_2 began at 575° . The oxide horizontals for these two compounds appeared at about the same temperatures as that of CeO_2 .

Uranium(VI) nitrate hexahydrate began to lose water at 30° and gave a short horizontal which corresponded to anhydrous $UO_2(NO_3)_2$ at 200 to 220°. The oxide, U_3O_8 , appeared at 550°.

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SUMMARY

The thermolysis curves of the nitrates of lanthanum, cerium(III), praseodymium, neodymium, samarium, yttrium, scandium, thorium, uranium(VI) and zirconium were determined. The oxide levels were obtained in the temperature range of 450-830°.

RÉSUMÉ

Les courbes de thermolyse des nitrates de lanthane, cérium(III), praséodyme, néodyme, samarium, yttrium, scandium, thorium, uranium(VI) et zirconium ont été établies. Les paliers des oxydes sont atteints entre 450° et 830°.

ZUSAMMENFASSUNG

Die Thermolyse-Kurven der Nitrate von Lanthan, Cer(III), Praseodym, Neodym, Samarium, Yttrium, Scandium, Thorium, Uran(VI) und Zirkonium wurden bestimmt. Die Oxydstufen wurden zwischen 450 und 830° erreicht.

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DETERMINATION OF MICRO-AMOUNTS OF BORON IN URANIUM METAL AND IN URANYL CHLORIDE SOLUTIONS

by

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Boron, if present with polyvalent ions in aqueous solution, is usually first separated by alcohol-distillation¹, then determined by suitable means. ANDERSON AND MOTTA² used the alcohol-distillation method for the determination of boron in uranium. RUSSELL³, in a comprehensive survey of the literature for the determination of boron in trace quantities, noted that the boron recoveries were not as complete as might be desired (repeated alcohol-distillations are required), but that the results were indicative of the amounts present.

SILVERMAN AND TREGO⁴ made a basic study of the effects of reagents on microamounts of boron and found that an alcohol-distillation was not necessary using the curcumin-acetone solution method. This direct determination procedure is now applied to the determination of micro-amounts of boron in uranium metal or in uranyl chloride solution. The presence of uranium necessitates changes in the amounts of the necessary reagents which permit the formation of an acetone-soluble uranium oxalate.

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