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THE THERMAL DECOMPOSITION OF BERKELIUM COMPOUNDS*

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ABSTRACT

The thermal decomposition of several Bk compounds was studied with 1-mg quantities of ^{249}Bk. Comparative studies were also done with selected lanthanide elements, employing the same quantities of material and the same preparatory methods. The decomposition of the nitrate, chloride, sulfate, and oxalate was studied in air, Ar, and H_2-Ar atmospheres. It was found that in atmospheres containing oxygen or when oxygen can be provided by the anion, the Bk behaved very similarly to Ce. In the absence of oxygen, there was a greater tendency for the Bk to behave like Tb. From the decomposition of the hydrated salts, values can be assigned for the coordination number of Bk.

INTRODUCTION

The thermal decomposition of many lanthanide and actinide compounds is reported in the literature. With the availability of high-purity lanthanides, several studies were made to compare the decomposition behavior between members of the series. Duval[1] has summarized much of this early work. In recent years there has been an effort to prepare milligram quantities of the transplutonium elements to permit physical and chemical studies of the actinide series. At the present time, milligram quantities of ^{249}Bk and ^{249}Cf have been obtained for research programs.

Of the actinide series, the transplutonium elements are of special interest for comparing their chemistry with that of the lanthanides. Although the aqueous chemistry of Am, Cm, and Cf is essentially limited to that of the trivalent ions, the tetravalent state of Am, Cm, and Bk is easily attained in the solid state and, under special conditions, CfO_2 can also be prepared[2]. In solid

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compounds of the lanthanides, only Ce can be readily obtained in the tetravalent state while Pr and Tb require strong oxidizing conditions to fully reach this valence state.

This paper presents some studies made on the thermal decomposition of ^{249}Bk compounds, using a 1-mg quantity of the element. Since it was not possible to perform chemical analyses on the Bk compounds, the results were compared to the decompositions of lanthanide compounds prepared in an identical fashion on a 1-mg level. The Bk data were then interpreted from the behavior of the lanthanide runs. Several of the Bk products were subjected to X-ray analysis to confirm that the final residue was either Bk_2O_3 or BkO_2. The radioactive decay of ^{249}Bk, which decays predominantly by a 114-keV beta emission, results in the appearance of the ^{249}Cf daughter at the rate of about 1.5% per week. Since the masses of the two elements are identical, the only difference in the weight data for a pure Bk sample versus a Bk-Cf mixture would occur when the stoichiometry in the particular compound differed for the two elements, and even then, an appreciable amount of Cf would be required to bring about a detectable weight change.

EXPERIMENTAL

A. Materials

The ^{249}Bk used in this study was produced in the HFIR at Oak Ridge and was separated from the lanthanides and the other actinide elements by Tramex solvent extraction, LiCl anion exchange, and chromatographic elution from a cation exchange column with α-hydroxyisobutyrate. Additional purification was carried out by ion exchange using specially purified reagents, ion exchange resins, and preleached quartzware. Details of the purification scheme have been reported[3]. Samples of the product were taken for impurity analysis by spark-source mass spectrometry, which showed that the product contained <0.02 atom % of the lanthanides and was >99.8 atom % pure with regard to the total cation impurities.

All reagents were of high purity (Baker Ultex acid, recrystallized reagent-grade oxalic acid), and only triply distilled water was used. The Gd, Tb, and Ce compounds were prepared in an identical manner as described for the Bk compounds, starting with the oxides supplied by Research Chemicals (99.9 to 9[illegible]%). 99.99

B. Apparatus

Thermogravimetry studies were made with a Cahn RG Electrobalance using programmed heating rates of 1 to 5 degrees/minute. The microbalance was housed in a vacuum chamber which was connected to a 1-in.-diameter ceramic furnace tube. The system permitted thermal decomposition studies in a static or a flowing atmosphere, as well as in vacuum. Temperature measurements were made inside the furnace tube approximately 3 mm below the sample cup, with a platinum-10% rhodium thermocouple. The entire system was contained inside of a two-compartment glove box, which permitted isolation of the balance assembly from the sample handling area.

As a compromise, the sample containers were constructed of quartz. It was necessary to maintain a suspension system and sample container with a low mass but moderately large volume. Several matched quartz sample cups were made that had a circular opening of 5 mm and a height of 6 mm. The large sample volume was necessary to permit the transfer and evaporation of liquid samples and the dissolution of the oxides in the cup.

C. Sample Preparation

Since only 1 mg of Bk was available for the study, it was necessary to ensure that all transfers and recovery operations were quantitative. This necessitated the transfer of the preparation either as a solution or a slurry to the sample cup used for the thermogravimetry work. The excess water was carefully evaporated by focusing a jet of argon over the surface of the cup at room temperature until a solid was obtained. The sample cup was then placed in position on the balance, the system closed, and the desired atmosphere then obtained. Generally, the sample was purged with a flowing gas at room temperature until a constant weight was obtained, indicating that the remaining ~~amount of~~ surface water had been removed. The sample was then heated and the weight loss recorded. In some cases, where it was desired to ensure a particular atmosphere, the system was evacuated and backfilled with the desired gas. In several experiments, the atmospheres were changed at elevated temperatures by thoroughly purging the system while maintaining an isothermal condition.

When the experiment was finished, the resulting product was dissolved in the sample cup with HNO_3, HCl, HCl-HF, or HNO_3-HF. The choice of acids was determined by the ease of dissolving the product and by the subsequent use of the solution. The dissolution of BkO_2 often necessitated the use of small amounts of HF (1:50) in addition to the 6-10 M acid. The difficulty in dissolving BkO_2 is characteristic of the isostructural (fluorite crystal structure) actinide dioxides, and the fluoride ion is commonly used to dissolve high-density ThO_2 or PuO_2. Dissolution of the product in HCl or HNO_3 and evaporation of the solution to dryness provided another sample for study. In these cases, the resulting salt was dissolved in 50-100 μℓ of water and reevaporated to ensure removal of excess acid. In cases where special or additional treatment was required, the solutions were transferred to a semimicro quartz cone or to a platinum crucible.

When it became necessary to remove extraneous cations or anions that were present, the Bk was either repeatedly fumed in a platinum crucible or passed through a micro anion exchange column. Small amounts of silica could be removed by fuming with HF, and fuming with H_2SO_4 provided the anhydrous sulfate salt. For preparing the oxalates, a conventional oxalic acid precipitation and washing technique was employed, and the precipitate was transferred to the sample cup as a slurry.

The quantity of Bk present in the samples was determined by one or a combination of the following methods: (1) a radiochemical analysis using a windowless proportional counter; (2) a gravimetric analysis based on the mass of the Bk_2O_3 or BkO_2 product; (3) an analysis of the weight change observed during the conversion between the two oxide stoichiometries. Whenever the situation permitted, the samples were placed in precalcined and preweighed sample cups to accurately determine the mass of the products.

D. X-ray Diffraction

Samples of the residues were taken for X-ray diffraction analysis by using a quartz fiber to remove 1-10 μg of material. These samples were then placed in conventional 0.2-mm X-ray capillaries and powder patterns obtained with a 57.3-mm-diameter Philips Norelco (Debye-Scherrer type) camera, using a microfocus X-ray generator and nickel filtered copper radiation.

RESULTS AND DISCUSSION

Three lanthanides were chosen for comparing the decomposition of their compounds with the corresponding compounds of Bk. Cerium was selected because of its comparable III-IV oxidation states and the similar stabilities of CeO_2 and BkO_2. Gadolinium was chosen because the ionic radius of Gd^{3+} is very close to that of Bk^{3+}, as calculated from the lattice parameters of the isomorphic sesquioxides, and because Gd can be considered as possessing a "pure" trivalent state. Terbium was used because it is the electronic counterpart of Bk in the lanthanide series.

Of the various compounds prepared and studied, the hydrated $Bk(NO_3)_3$ and $BkCl_3$ salts were the easiest to prepare and the results of the $Bk(NO_3)_3$ salt were the most straightforward to interpret. With some of the salts or compounds, it was necessary to rely on published results on the lanthanides to assign the stepwise decomposition to specific chemical reactions. In addition to carrying out the decompositions in air atmospheres, argon and H_2-Ar atmospheres were also used in an effort to maintain the trivalent state of Bk as much as possible.

The light-green, hydrated $Bk(NO_3)_3$ salt was easily obtained by evaporation of dilute Bk-HNO_3 solutions. A comparison of the Bk $(NO_3)_3$ decomposition in air to the decomposition of the trivalent, hydrated nitrate salts of Ce, Gd, and Tb demonstrated that the Bk salt behaved very similarly to the cerium salt. The behavior was predictable since the stabilities of BkO_2 and CeO_2 have been shown to be similar and the III-IV oxidation potential of Bk is nearly identical with that for Ce[4]. From the thermal decomposition curves for the nitrate salts it can be seen that, after the loss of the hydrated water, both Ce nitrate and Bk nitrate had a much steeper weight loss curve and their decomposition occurred at lower temperatures than was observed for the Gd and Tb salts. The decomposition curves also indicate the formation of oxynitrate intermediates for Gd and Tb but show very little, if any, evidence for the formation of Bk or Ce oxynitrates. Decomposition of the nitrate salts in air produced CeO_2 and BkO_2 at 400-500°C, Gd_2O_3 at 600°, and after cooling to room temperature, the Tb product was found to be Tb_4O_7.

The decomposition of the hydrated nitrate salts in argon or H_2-Ar was very similar to that in air. The curves for the runs in H_2-Ar did have a slight inflection to indicate the formation of an oxynitrate intermediate for Ce and Bk, but the magnitude of the inflection indicated that formation of the intermediate was not quantitative. Although the sesquioxides were the final products in the H_2-Ar atmospheres it appears likely that the higher oxides of Ce and Bk were reduced by the H_2 at an elevated temperature (>700°C). It would be difficult to prevent oxidation of the Ce and Bk during the decomposition of the nitrate salts, since oxygen and nitrogen oxides are generated in situ.

From the decomposition curves it can be seen that the water of hydration is lost below 300°C. The existence of the anhydrous salt or intermediate hydrates was indicated only by inflections in the curves. Using these thermal analysis curves, the compositions of the starting materials were calculated to be $Gd(NO_3)_3 \cdot 4H_2O$, $Tb(NO_3)_3 \cdot 4H_2O$, $Bk(NO_3)_3 \cdot 4H_2O$, and $Ce(NO_3)_3 \cdot 6H_2O$.

The hydrated $BkCl_3$ salts were also obtained by evaporating an aqueous solution in the sample cup. The curves obtained for the decomposition of the Bk chloride in air tended to be more similar to the curves for the Gd and Tb chlorides, as compared to the behavior of the nitrate salts. However, the Bk salt decomposed at a lower temperature and the Bk curve indicated only a very slight inflection in the temperature region for conversion of an oxychloride to the oxide. The interpretation is that, as a result of the stability of CeO_2 and BkO_2, these dioxides are readily formed at the lower temperatures in the air atmosphere. In Ar or H_2-Ar atmospheres, inflections in the curve at the 600-900°C region indicated that a Bk oxychloride may have been formed, whereas with Ce only a slight inflection appeared in this region. Calculations made from the weight losses indicated that, after the loss of water, Ce converted rapidly to the dioxide whereas the other salts formed $M_2OCl \cdot 2MCl_3$ and M_2OCl as intermediates. The decomposition mechanism of the lanthanide chlorides has been reported[5]. The data obtained in this work established that all of the starting salts were hexahydrates.

The oxalates of Ce, Gd, Tb, and Bk were each prepared on a 1-mg level, using oxalic acid as the source of the oxalate ion. After the precipitates had been washed, the material was transferred to the sample cups and slowly dried at room temperature under a stream of Ar. Examination of the curves for the oxalate decomposition in air showed that the oxalates of Ce and Bk decomposed at considerably lower temperatures in a single step, as compared with the oxalates of Gd and Tb. In Ar or H_2-Ar atmospheres, the decomposition curves of all four oxalates were very similar and the decomposition of the oxalate anion began at ~350°, with inflections in the curve indicating the existence of intermediate products before the oxides are obtained. These intermediates have been reported to be subcarbonates[6] formed during the decomposition. In the inert or reducing atmospheres, a carbonaceous product was obtained in the product and, to obtain the pure oxide, it was necessary to heat the material above 800°C in oxygen-containing atmospheres.

The initial oxalates of Ce, Gd, Tb, and Bk were all tetrahydrates, which differ from the decahydrates previously reported in the literature for these lanthanides[1]. The difference observed in this work may have resulted from dehydration during the drying procedure at room temperature as these higher hydrates are reported to readily lose water at lower (<100°C) temperatures. There may also be some question to whether these materials are true hydrates, as air drying has reportedly caused a fluctuation in the number of water molecules found in the starting materials[1].

The sulfates of trivalent Ce, Gd, Tb, and Bk were prepared by fuming 1-mg amounts of the cation in H_2SO_4 to dryness at 300°C. The solid hydrates were obtained by dissolving the residue in water and slowly evaporating the solution to constant weight under an argon stream. All four salts prepared in this manner contained excess water and indicated abnormally high values for the hydrates. In the thermal decomposition curves, the salts showed an inflection about 100°C, and a more reasonable value for the hydrate could be obtained by considering only the water that was lost above this temperature. Using this method, the hydrates were calculated to be $Ce_2(SO_4)_3 \cdot 8H_2O$, $Gd_2(SO_4)_3 \cdot 12H_2O$, $Tb_2(SO_4)_3 \cdot 12H_2O$, and $Bk_2(SO_4)_3 \cdot 12H_2O$. The values listed here for Ce and Gd are higher than previously reported for the hydrates, where a penta- and an octahydrate were found[7]. However, in that study, the hydrated salts were washed with ethanol, ground to a fine powder, and then air dried for several hours.

The decomposition of the sulfate anion was examined in air, Ar, and H_2-Ar. In H_2-Ar the four sulfates decomposed in a single step, with the change occurring between 500 to 680°C for Ce and Bk and 600 to 800°C for Gd and Tb. In air or Ar atmospheres, the Ce and Bk sulfates again decomposed in a single step but at slightly higher temperatures (700 to 900°C). With Gd and Tb, a two-step decomposition was observed for the sulfate anion, with an oxysulfate, $(M_2O_2(SO_4))$, forming between 800 to 900°C, which then converted to the oxide at 950 to 1150°C. It was evident that the H_2 present in the H_2-Ar atmospheres reacted with the sulfate anion to yield the oxide at lower temperatures.

Several of the Bk oxide products were examined by X-ray diffraction analysis. In air or Ar atmospheres, the products were BkO_2 and values for the fcc lattice parameters ranged from 5.320 to 5.332 Å. When H_2-Ar atmospheres were employed, the final products were Bk_2O_3 and values for the bcc lattice parameter ranged from 10.86 to 10.92 Å. The lattice parameters for the oxides are in agreement with the values previously established for the system[8,9].

The results of the thermal decomposition studies on these compounds can be summarized by stating that the Bk compounds behaved very similarly to the corresponding Ce compounds when oxygen was present in the atmosphere or when oxygen was readily provided by the anion (i.e. nitrate salts). In inert or reducing atmospheres, the Bk compounds tended to decompose like the corresponding Tb compounds, or at least in a manner which is intermediate between the Ce and Tb compounds.

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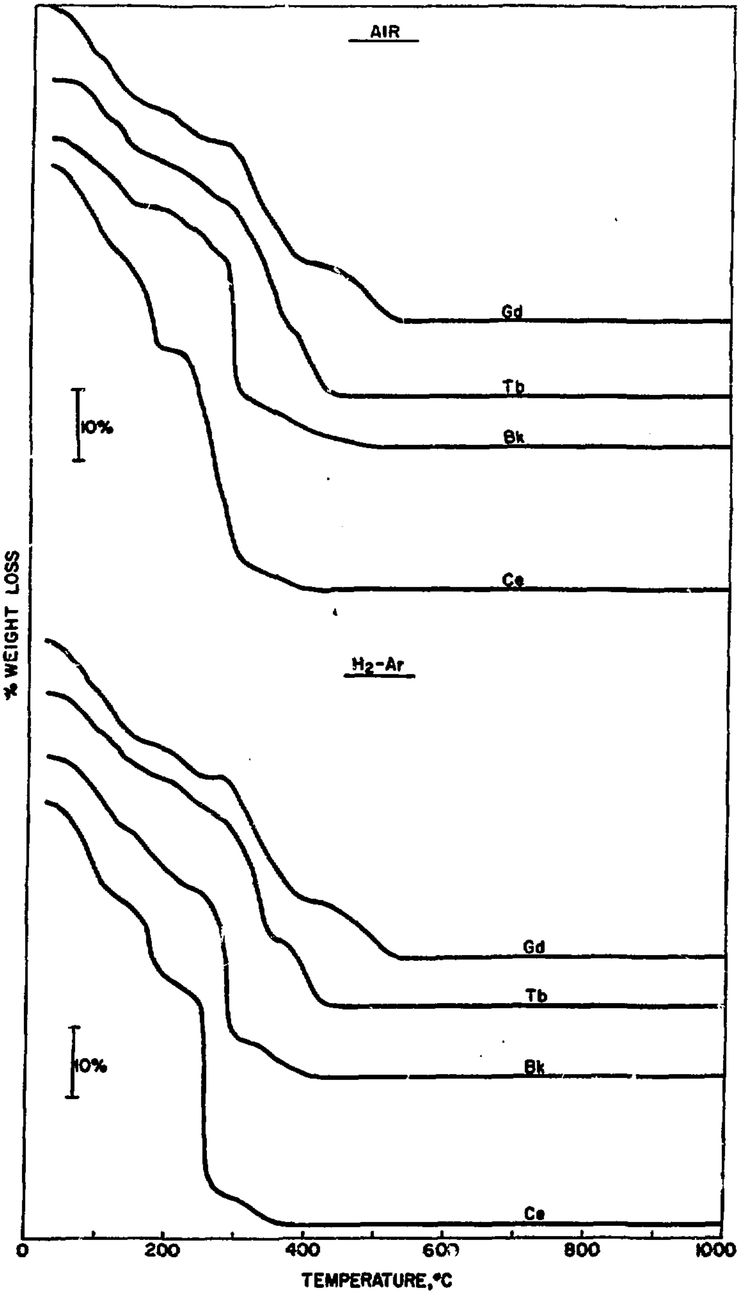

THERMAL DECOMPOSITION OF Ce, Gd, Tb AND Bk NITRATES

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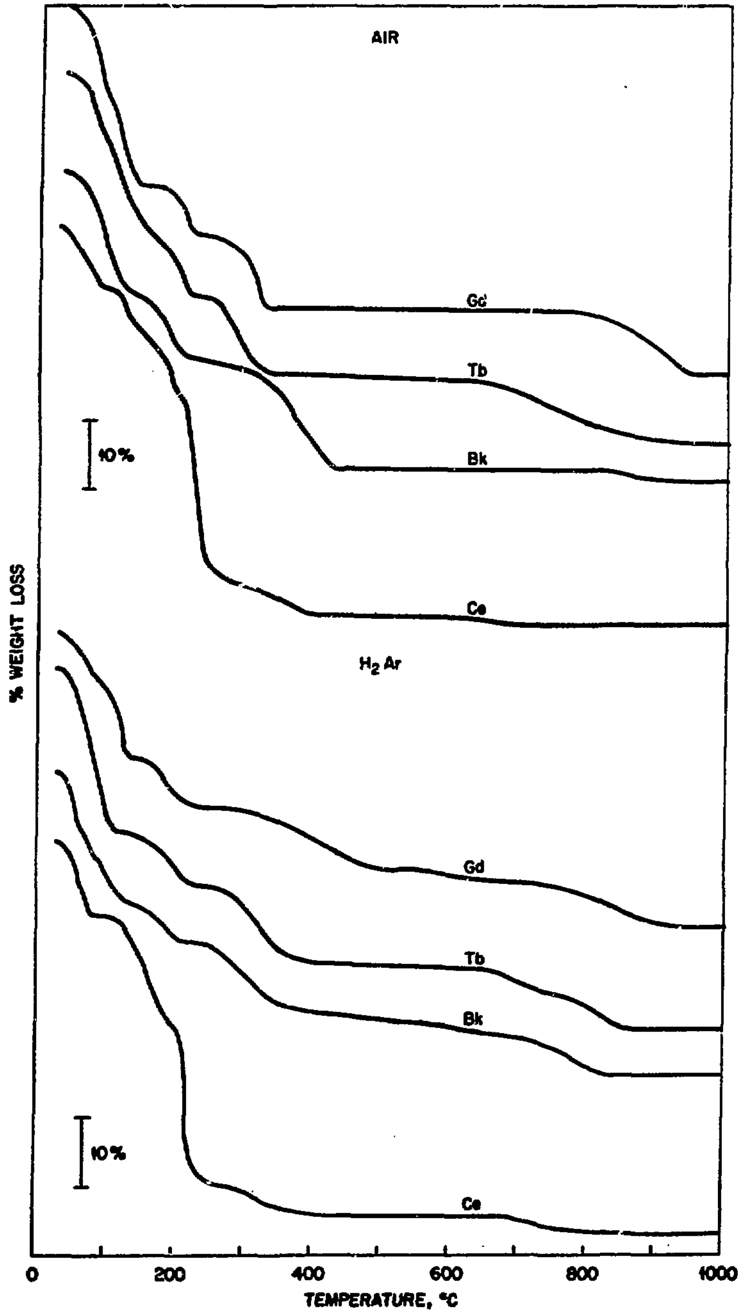

THERMAL DECOMPOSITION OF Ce, Gd, Tb AND Bk CHLORIDES

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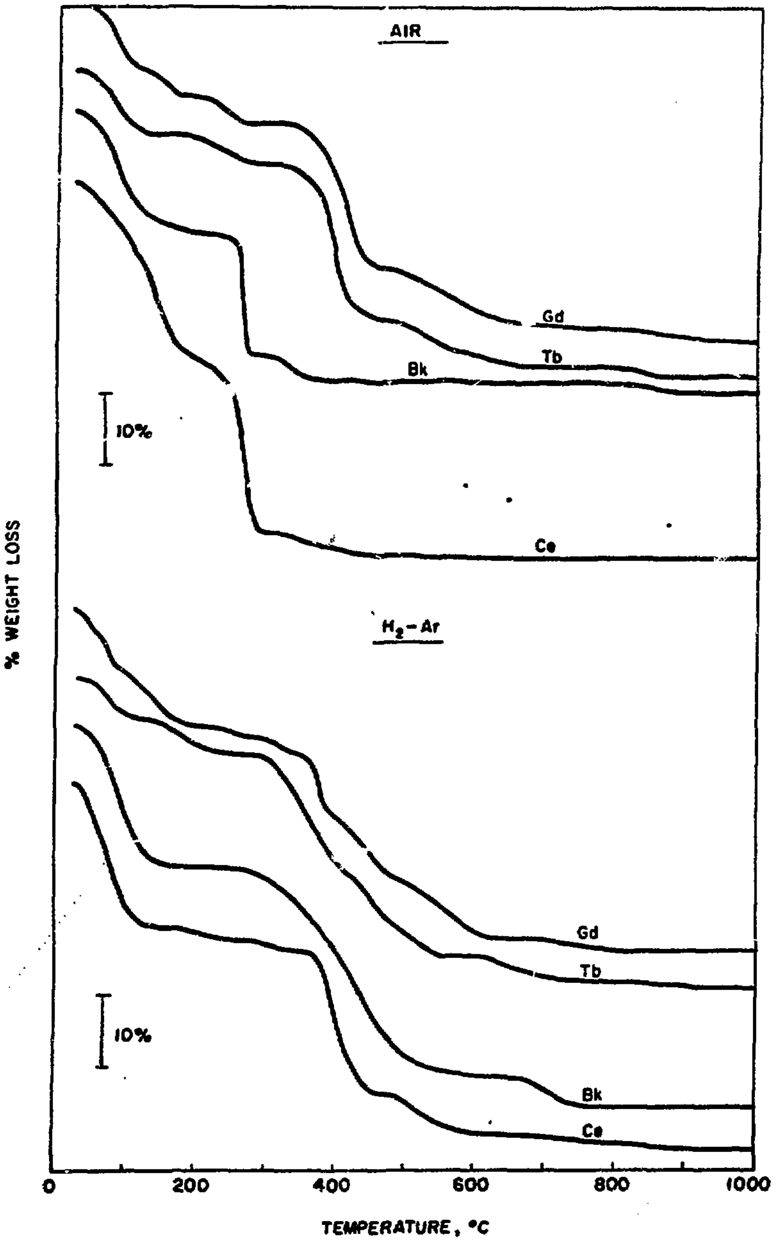

THERMAL DECOMPOSITION OF Ce,Gd,Tb AND Bk OXALATES