The Preparation and Thermal Decomposition of the Carbonates of Tb, Dy, Ho, Er, Tm, Yb, Lu, Y, and Sc

by

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The Preparation and Thermal Decomposition of the Carbonates of Tb, Dy, Ho, Er, Tm, Yb, Lu, Y, and Sc

ABSTRACT

The preparation and thermal decomposition of the carbonates of the lighter lanthanons, La through Gd, were described at the 1963 Third Rare Earth Conference in Clearwater, Florida. This paper presents the results of the extension of those studies to the heavier lanthanons, and yttrium and scandium.

The hydrated carbonates were prepared by precipitation from a homogeneous aqueous solution by thermal decomposition of the corresponding trichloroacetates as previously described. In all cases except for scandium and lutetium, the ratio of carbonate to oxide was 2.93 or greater, the ratio of water to oxide was between 2.1 and 2.3, and the compounds were isostructural with \( \text{Nd}_2(\text{CO}_3)_3 \cdot 2\text{H}_2\text{O} \). For lutetium, the compound had corresponding ratios of 2.99 and 5.2 and the structure was different from the others. For scandium, the compound with the highest carbonate content had a ratio of carbonate to oxide of 2.25. The thermal decomposition studies were done on the dicarbonate, \( \text{Sc}_2 \text{O}(\text{CO}_3)_2 \cdot 2\text{H}_2\text{O} \).

The thermal decomposition of these compounds was studied with a recording vacuum thermobalance in vacuum, carbon dioxide, and water vapor. Except for lutetium and scandium the decomposition proceeded by the steps \( \text{Me}(\text{CO}_3)_3 \cdot x\text{H}_2\text{O} \rightarrow \text{Me}(\text{CO}_3)_3 \rightarrow \text{intermediate} \rightarrow \text{Me}_2\text{O}_3 \) as shown by corresponding plateaus in the pyrolysis curves. The intermediate was the dioxymonocarbonate for terbium and dysprosium. For Ho through Yb and for Y the intermediate contained less carbonate than the dioxy-monocarbonate. No intermediate carbonate was detected for lutetium. The plateau for the intermediate was shorter for the higher atomic number elements. The temperature of decomposition of the normal carbonates under 500 mm pressure of carbon dioxide was about 500°C with no marked trend with atomic number. For the intermediate there was a definite trend toward lower decomposition temperatures at higher atomic numbers except for ytterbium, which was out of place. Yttrium carbonate was similar to holmium and erbium carbonates in its behavior.
Introduction - This paper is a continuation of the work described at
the Third Rare Earth Conference on the preparation and thermal decom-
position of the carbonates of the lighter lanthanons, La through Gd (1).
Here results are reported for the carbonates of the heavier lanthanons,
Tb through Lu plus yttrium and scandium.

Compound Preparation - The normal sesquicarbonates were prepared by
precipitation from homogeneous solution of the corresponding trichloro-
acetates under carbon dioxide pressure as previously described (1). In
the case of scandium, even at carbon dioxide pressures as high as 800
psig and temperatures as low as 67°C it was not possible to obtain the
sesquicarbonate, and the product was intermediate between the sesqui-
carbonate and the monoxydicarbonate. The pyrolysis experiments for
scandium carbonate were done on the monoxydicarbonate.

As was done previously (1), the carbonates were analyzed by con-
ventional combustion analysis for carbon and hydrogen and ignition of
the final oxide to constant weight in oxygen at 1000°C. The results
are shown in Table I. Differences of 0.02 or 0.03 from the theoretical
3.00 for the CO$_2$/R$_2$O$_3$ ratio are not considered significant. By this
criterion, Dy, Er, Yb, and Y carbonates show a slight but significant
deficiency of carbonate. Scandium forms the monoxydicarbonate.

The hydrated carbonates were examined by X-ray diffraction. The
dihydrates were found to be isostructural with Nd$_2$(CO$_3$)$_3$·2H$_2$O. The
lutetium carbonate gave a new pattern.

Thermal Decomposition - The thermal decomposition of these carbonates
was studied at a rate of temperature rise of 36°/hour in vacuum, in
water vapor, and in carbon dioxide with a recording vacuum thermo-
balance. (2). The resulting curves are shown in Figures 1-9. Except
for scandium and lutetium, which will be discussed separately below,
they are very similar to the analogous curves obtained for the thermal
decomposition of the lighter lanthanon carbonates. In vacuum there
is an initial loss of weight leading to a more or less well-defined
plateau at a weight loss corresponding approximately to the anhydrous
normal carbonate. In water vapor there is no evidence for any inter-
mediate hydrates between the dihydrate and the anhydrous carbonate.
In carbon dioxide decomposition of the anhydrous carbonates proceeds through at least one intermediate stage. The approximate compositions of these intermediate stages are shown in Table II. These portions of the pyrolysis curves are shown on an expanded scale in Figure 10. In general, as the atomic weight increases the following things are observed: a) the slope of the curve at the fastest rate of decomposition of the normal carbonate decreases, b) the temperature in this region increases, c) the carbon dioxide content of the intermediate phase (2nd intermediate phase for Dy) decreases, and d) the temperature of decomposition of the intermediate phase decreases, except for Yb, which is above 1m.

Yttrium carbonate is very similar to holmium and erbium carbonates, as would be expected from other similarities between yttrium and these elements.

Lutetium carbonate differs from the other members of the series in several respects. It forms a hydrate with about 5 waters of hydration instead of 2, and there are slight breaks in the curve for decomposition in water vapor at compositions of about 3.2 and 2.5 waters of hydration, respectively. The pyrolysis curve in carbon dioxide does not show any intermediate phase between the normal carbonate and the oxide.

The pyrolysis curves for scandium carbonate are for a composition which is nominally the monoxidecarbonate with 4 waters of hydration. The interpretation of these curves is obscure.

In all cases the oxide formed by thermal decomposition of the carbonate in vacuum, water vapor, or carbon dioxide was the sesquioxide, even for terbium.

Some of the hydrated carbonates have been examined optically and found to be anisotropic.

Samples of the anhydrous carbonates and of the materials at the various plateaus will be taken and examined by X-rays and by optical microscopy. The results will be reported at the meeting.

Discussion - The preparation and thermal decomposition of the carbonates of the heavy lanthanons and of yttrium and scandium have been studied by Strouth (3). She used the trichloroacetate method of
preparation for all of them except scandium, which was prepared by repeated washing of the ammonium scandium double carbonate. The preparations were carried out at atmospheric pressure and resulted in the normal sesquicarbonates for yttrium and terbium and in the monoxide-dicarbonates for dysprosium, holmium, erbium, thulium, ytterbium, lutetium, and scandium. For the normal carbonates of yttrium and terbium she found the 15-hydrate and tri-hydrate, respectively. She found by differential thermal analysis that the normal carbonates decomposed according to

\[ \text{Me}_2(\text{CO}_3)_3 \rightarrow \text{Me}_2\text{O}(\text{CO}_3)_2 \rightarrow \text{Me}_2\text{O}_2\text{CO}_3 \rightarrow \text{Me}_2\text{O}_5. \]

Although she did not isolate the dioxymonocarbonates of Dy, Ho and Er, she did report the isolation of this compound for Y, Tb, Tm, Yb, and Lu.

Wendlandt and George (4) have also reported work on the preparation and thermal decomposition of several rare earth carbonates, but the report gives very few details of their work.

Yttrium carbonate has been studied by Domingues, Wilfong, and Furlong (5). They reported \( \text{Y}_2(\text{CO}_3)_3 \cdot 3\text{H}_2\text{O} \) as their starting material, and they found evidence for both the oxydicarbonate and the dioxymonocarbonate intermediate compositions.

In the work reported in this paper the ability to prepare the normal sesquicarbonates of all of the rare earths by the technique described herein has been demonstrated. The dioxymonocarbonate of Tb and Dy was observed and isolated, but this was not so for the succeeding heavy lanthanons, Y, and Sc. Only decomposition products intermediate between the dioxymonocarbonate and the oxide were observed for Ho, Er, Tm, Yb, and Y; however, higher \( \text{CO}_2 \) pressures conceivably would produce the dioxymonocarbonates of these elements. No monoxydicarbonate was observed except with Sc, for which it was the starting material.

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BIBLIOGRAPHY


Table I
Analysis of Rare Earth Carbonates Used in Pyrolysis Experiments

<table>
<thead>
<tr>
<th>Element</th>
<th>CO₂/R₂O₃</th>
<th>H₂O/R₂O₃</th>
</tr>
</thead>
<tbody>
<tr>
<td>Tb*</td>
<td>2.97</td>
<td>2.1</td>
</tr>
<tr>
<td>Dy</td>
<td>2.95</td>
<td>2.3</td>
</tr>
<tr>
<td>Ho</td>
<td>2.98</td>
<td>2.1</td>
</tr>
<tr>
<td>Er</td>
<td>2.96</td>
<td>2.2</td>
</tr>
<tr>
<td>Tm</td>
<td>2.99</td>
<td>2.1</td>
</tr>
<tr>
<td>Yb</td>
<td>2.96</td>
<td>2.2</td>
</tr>
<tr>
<td>Lu</td>
<td>2.99</td>
<td>5.2</td>
</tr>
<tr>
<td>Y</td>
<td>2.93</td>
<td>2.1</td>
</tr>
<tr>
<td>Sc</td>
<td>2.04</td>
<td>4.0</td>
</tr>
</tbody>
</table>

*For terbium the oxide was determined by difference.

Table II
Intermediate Solid Phases
in Decomposition of Rare Earth Carbonates in Carbon Dioxide (500 mm)

<table>
<thead>
<tr>
<th>Element</th>
<th>1st Stage</th>
<th>2nd Stage</th>
</tr>
</thead>
<tbody>
<tr>
<td>Tb</td>
<td>Tb₂O₂.₀₂(CO₃)₀.₉₈</td>
<td>Dy₂O₂.₀₆(CO₃)₀.₉₄</td>
</tr>
<tr>
<td>Dy</td>
<td>Dy₂O₁.₈₈(CO₃)₁.₀₂</td>
<td></td>
</tr>
<tr>
<td>Ho</td>
<td>Ho₂O₂.₁₁(CO₃)₀.₉₉</td>
<td></td>
</tr>
<tr>
<td>Er</td>
<td>Er₂O₂.₁₂(CO₃)₀.₉₉</td>
<td></td>
</tr>
<tr>
<td>Tm</td>
<td>Tm₂O₂.₁₆(CO₃)₀.₉₂</td>
<td></td>
</tr>
<tr>
<td>Yb</td>
<td>Yb₂O₂.₄₈(CO₃)₀.₅₂</td>
<td></td>
</tr>
</tbody>
</table>
Figure Captions

Fig. 1 Terbium Carbonate, Tb$_2$(CO$_3$)$_3$·2.1H$_2$O

Fig. 2 Dysprosium Carbonate, Dy$_2$(CO$_3$)$_3$·2.3H$_2$O

Fig. 3 Holmium Carbonate, Ho$_2$(CO$_3$)$_3$·2.1H$_2$O

Fig. 4 Erbium Carbonate, Er$_2$(CO$_3$)$_3$·2.2H$_2$O

Fig. 5 Thulium Carbonate, Tm$_2$(CO$_3$)$_3$·2.1H$_2$O

Fig. 6 Ytterbium Carbonate, Yb$_2$(CO$_3$)$_3$·2.2H$_2$O

Fig. 7 Lutetium Carbonate, Lu$_2$(CO$_3$)$_3$·5.2H$_2$O

Fig. 8 Yttrium Carbonate, Y$_2$(CO$_3$)$_3$·2.1H$_2$O

Fig. 9 Scandium Carbonate, Sc$_2$O(CO$_3$)$_3$·4H$_2$O

Fig. 10 Thermal Decomposition of Rare Earth Carbonates in ~500 mm Carbon Dioxide
Fig. 1 Terbium Carbonate, $\text{Tb}_2\text{(CO}_3\text{)}_3 \cdot 2\text{H}_2\text{O}$

- **VACUUM**
- $\text{CO}_2$ ($\sim$ 500 MM)
- $\text{H}_2\text{O}$ ($\sim$ 20 MM)
Fig. 2 Dysprosium Carbonate. Dy$_3$(CO$_3$)$_2$·2.3 H$_2$O

- **VACUUM**
- **CO$_2$ (≈ 500 MM)**
- **H$_2$O (≈ 20 MM)**

**Graph Details:**
- **Y-Axis:** Per cent weight loss
- **X-Axis:** Temperature (°C)
- **Legend:**
  - Open circle for VACUUM
  - Triangle for CO$_2$ (≈ 500 MM)
  - Filled circle for H$_2$O (≈ 20 MM)
Fig. 3 Holmium Carbonate, Ho$_2$(CO$_3$)$_3$·21 H$_2$O

- VACUUM
- CO$_2$ (≈ 500 MM)
- H$_2$O (≈ 20 MM)
Fig. 4: Erbium Carbonate, Er₂(CO₃)₃·2.2 H₂O

- VACUUM
- CO₂ (≈ 500 MM)
- H₂O (≈ 20 MM)
Fig. 5  Thulium Carbonate. \( \text{Tm}_2(\text{CO}_3)_3 \cdot 2.1 \text{H}_2\text{O} \)

- O VACUUM
- ▲ \( \text{CO}_2 \) (≈500 MM)
- ● H\_2\text{O} (≈20 MM)
Fig. 6 Ytterbium Carbonate, Yb₂(CO₃)₃·2.7 H₂O

- ○ ○ VACUUM
- △ △ CO₂ (≈ 500 MM)
- ● ● H₂O (≈ 20 MM)
Fig. 7 Lutecium Carbonate, \( \text{La}_2\text{CO}_3 \cdot 5.7 \text{H}_2\text{O} \)

- **VACUUM**
- **\( \text{CO}_2 \) (\( \sim 500 \text{ MM} \))**
- **\( \text{H}_2\text{O} \) (\( \sim 20 \text{ MM} \))**
Fig. 8 Yttrium Carbonate, $\text{Y}_2\text{CO}_3 \cdot 2\text{H}_2\text{O}$

- **Vacuum**
- $\text{CO}_2$ (≈ 500 MM)
- $\text{H}_2\text{O}$ (≈ 20 MM)
Fig. 9 Scandium Carbonate, $\text{Sc}_2\text{O}_2\text{CO}_3 \cdot 4 \text{H}_2\text{O}$

- **VACUUM**
- **$\text{CO}_2$ (\(\sim\) 500 MM)**
- **$\text{H}_2\text{O}$ (\(\sim\) 20 MM)**
Fig. 10 Thermal Decomposition of Rare Earth Carbonates in 500 mm Carbon Dioxide

- Tb
- Dy
- Ho
- Er
- Tm
- Yb (Dashed curve is with H₂O present)
- Lu
- Y
- Sc