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A THERMOGRAVIMETRIC STUDY OF THE ADIPATES AND SEBACATES OF PRASEODYMIUM AND NEODYMIUM[*]

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ABSTRACT

A study of the thermal decomposition, in air, of praseodymium and neodymium adipate and sebacate has suggested the decomposition pattern which follows (An represents either adipate or sebacate). The compounds were prepared by homogeneous precipitation.

For the adipates formed at pH greater than 5 as well as for the sebacates precipitated at any pH:

$$\begin{tikzcd}
\mathrm{Ln_2(An)_3} \arrow[r] & \mathrm{Ln_2O(An)_2} \arrow[r] & \mathrm{Ln_2O_{1.5}(An)_{1.5}} \arrow[r] & \mathrm{Ln_2O_2(An)} \arrow[dd] \\
\mathrm{Pr_6O_{11}} & & & \\
& \mathrm{Ln_2O_{2.5}(CO_3)_{0.5}} \arrow[ul] \arrow[dl] & & \mathrm{Ln_2O_2CO_3} \arrow[ll] \\
\mathrm{Nd_2O_3} & & &
\end{tikzcd}$$

For the adipates formed at pH less than 5:

$$\begin{tikzcd}
\mathrm{Ln_2(An)_3} \arrow[r] & \mathrm{Ln_2O_{0.5}(An)_{2.5}} \arrow[r] & \mathrm{Ln_2O_{0.5}(CO_3)_{0.5}(An)_2} \arrow[d] \\
\mathrm{Ln_2O_2CO_3} \arrow[dr] \arrow[ddr] & \mathrm{Ln_2O_{0.5}(CO_3)_{2.5}} \arrow[l] & \mathrm{Ln_2O_{0.5}CO_3(An)_{1.5}} \arrow[l] \\
& \mathrm{Pr_6O_{11}} & \\
& \mathrm{Nd_2O_3} &
\end{tikzcd}$$

The sebacates were precipitated quantitatively at pH greater than about 5.1; precipitation of the adipates was incomplete even at values of pH as high as 8.8. The adipates were thermally stable up to 180°C whereas the sebacates underwent slow decomposition at temperatures close to 100°C.

INTRODUCTION

Thermal decomposition studies of lanthanide dicarboxylic acid salts have focused chiefly on the oxalates[1–12]. Investigations involving other lanthanide dicar-

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[*] This paper is based on a portion of the Ph.D. dissertation of A. M. Wynne, University of Massachusetts, Amherst, 1970.

boxylic salts have been carried out however. These include the decomposition in air of the malonates, succinates, glutarates, adipates, pimelates, suberates, azelates, and sebacates of Ce[13], Nd[14], and Eu[15], the malonates and succinates of all the lanthanides[16], Dy sebacate[17], and the fumarates and succinates of Gd[18], Dy and Ho[19], and Yb[20]. Decomposition in oxygen of the oxalates, malonates, and succinates of La, Ce, Pr, Nd, and Sm has also been studied[10].

In these investigations, all starting compounds were formed by heterogeneous precipitation. The identification of intermediate solid residues, where made, has been based generally on weight relationships taken from thermogravimetric curves obtained at a single heating rate. The latter has not always been specified.

This work involves a thermogravimetric study of homogeneously precipitated praseodymium and neodymium adipates and sebacates. Thermogravimetric curves obtained at different heating rates as well as isothermal decompositions, infrared absorption spectra, and elemental analyses have been used to identify intermediate solid residues. Information thus obtained has been utilized in postulating decomposition mechanisms.

EXPERIMENTAL

Materials

Praseodymium and neodymium solutions were prepared from the respective oxides. Both A. D. McKay and private stock samples were used. The former were at least 99.9% pure and the latter were known to contain no more than traces of other elements. The oxides were dissolved in a small amount of 15 M HNO_3, after which the solutions were diluted with water.

The dicarboxylic acids were Eastman White Label adipic and sebacic acids. Infrared spectra conformed to corresponding spectra in the Sadtler Index.

Baker Reagent Grade urea was used in all experiments.

The formation of precipitates

Precipitates were formed homogeneously by the hydrolysis of urea in 150–300 ml of aqueous solution. Concentrations of lanthanide ion were in the range 0.01–0.1 M. The mole ratio of lanthanide to dicarboxylic acid varied between 1:4.5 and 1:6. As little as 2 g or as much as 12 g of urea was used.

To neutralize any excess of HNO_3 used in dissolving the lanthanide oxide, the pH of the solution was adjusted to 3–3.5 with aqueous NH_3 prior to the hydrolysis of urea. Sebacic acid, largely undissolved at this point, dissolved completely before any metal dicarboxylate precipitate formed.

Decomposition of urea and, hence, neutralization of the solution was effected by keeping the solution at 100°C. Precipitation was stopped simply by cooling the solution. Once the mixture cooled to room temperature, its pH was measured and this value has been designated as the pH of precipitation. The pH of precipitation was controlled by the length of time the hydrolysis of urea was allowed to proceed after the first appearance of metal dicarboxylate precipitate, although no attempt was made to develop a quantitative relationship. Values of pH greater than 6.5 required the use of aqueous NH_3. However, the latter was not added until urea hydrolysis had brought the pH to at least six.

Each precipitate was collected by suction filtration and washed with large amounts of water to remove unreacted dicarboxylic acid. Since knowledge of the degree of hydration was not germane to this investigation, some precipitates were dried at 110°C, others were stored over Drierite, and still others were simply dried in air at ambient conditions.

Analytical methods

TG. Thermogravimetric analyses were done using a Cahn RG Automatic Electrobalance, Model RG 2000. Samples were placed in a platinum boat suspended from a platinum wire in a Vycor tube. The latter was enclosed in a Marshall high temperature furnace.

Temperature was controlled by an F & M model 240 Power Proportioning Temperature Programmer and measured using a chromel–alumel thermocouple. The latter was mounted in a separate well within the Vycor tube close to the sample. The difference in temperature between the well and the body of the tube was found to be insignificant. Temperature and weight data were recorded on a Houston Instrument Model HR-100 X–Y Recorder.

All thermogravimetric curves were obtained in air at atmospheric pressure. No effort was made to purge the system of evolved gases during a run. Since the Cahn electrobalance is characterized by significant electronic noise at atmospheric pressure, rather large samples (i.e., approximately 25 mg) were decomposed in most cases and the instrument was operated at low sensitivity.

For easier comparison, all thermogravimetric curves have been reproduced in terms of relative weight. Relative weight 1.000 has been assigned to anhydrous starting material.

IR. Infrared spectra were obtained with a Perkin–Elmer Model 137 NaCl Spectrophotometer. Decomposition residues were run in KBr discs.

Elemental analyses. Analyses for metal, carbon, hydrogen, and, in some cases, oxygen were provided by the Office of Research Services, University of Massachusetts, Amherst, Mass., under the direction of the late Mr. Charles F. Meade.

RESULTS AND DISCUSSION

As expected, the value of pH at which precipitation started was a function of concentration. In general, the sebacates first appeared at pH about 3.9; adipates at pH about 4. Precipitation of the lanthanide sebacates was complete at pH greater than about 5.1. Quantitative precipitation of the lanthanide adipates was never achieved, even at pH values as high as 8.8.

Thermogravimetric curves for $Pr_2(C_6H_8O_4)_3$ and $Nd_2(C_6H_8O_4)_3$, shown in Figs. 1–4, indicate clearly that each decomposition involved a number of overlapping steps. Although the overall conversion was from $Ln_2(C_6H_8O_4)_3$ to the expected Pr_6O_{11} and Nd_2O_3, the identification of intermediate forms can not be unequivocal.

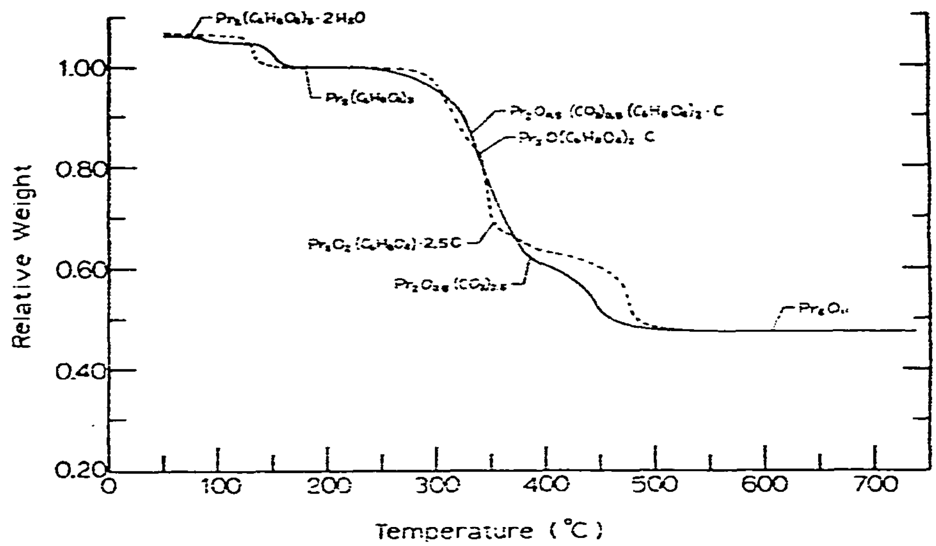


Fig. 1. Thermogravimetric curves for praseodymium adipate in air at atmospheric pressure. Curve ——————: 4.22 (pH of Pptn.); 23.8 (weight at 180°C, mg); 0.5 (heating rate, °C min^{-1}). Curve – – – – –: 6 (pH of Pptn.); 23.3 (weight at 180°C, mg),; 0.5 (heating rate, °C min^{-1}).

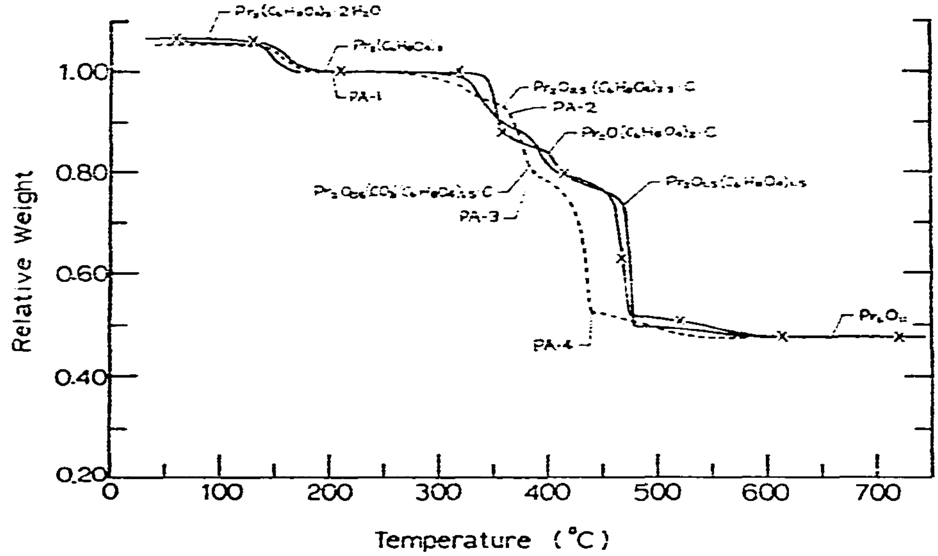


Fig. 2. Thermogravimetric curves for praseodymium adipate in air at atmospheric pressure. Curve – – – – –: 4.22 (pH of Pptn.); 24.2 (weight at 180°C, mg); 5 (heating rate, °C min^{-1}). Curve ——————: 6 (pH of Pptn.); 25.0 (weight at 180°C, mg); 5 (heating rate, °C min^{-1}). Curve —×—×: 6 (pH of Pptn.); 24.2 (weight at 180°C, mg); 10 (heating rate, °C min^{-1}).

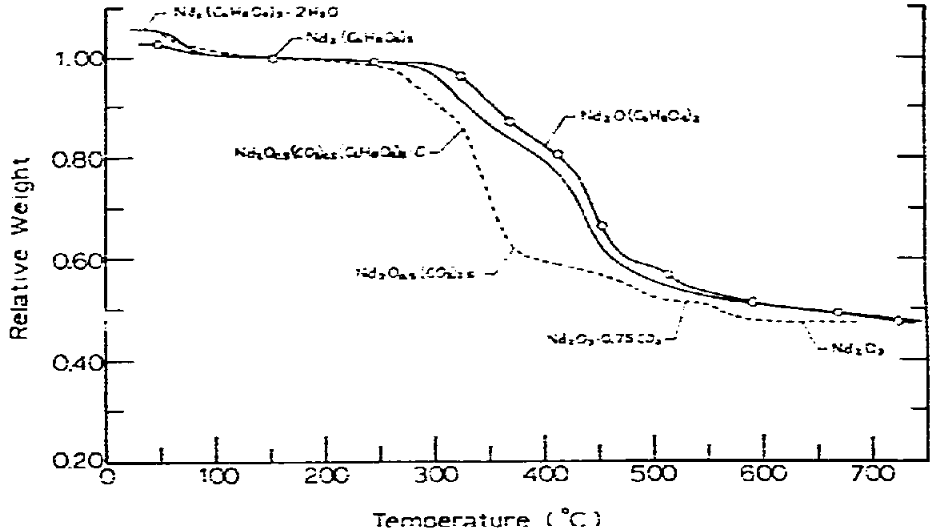


Fig. 3. Thermogravimetric curves for neodymium adipate in air at atmospheric pressure. Curve – – – – –: 4.02 (pH of Pptn.); 23.8 (weight at 180°C, mg); 0.5 (heating rate, °C min^{-1}). Curve ————: 5.36 (pH of Pptn.); 26.0 (weight at 180°C, mg); 0.5 (heating rate, °C min^{-1}). Curve o—o—o: 6.81 (pH of Pptn.); 24.0 (weight at 180°C, mg); 0.5 (heating rate, °C min^{-1}).

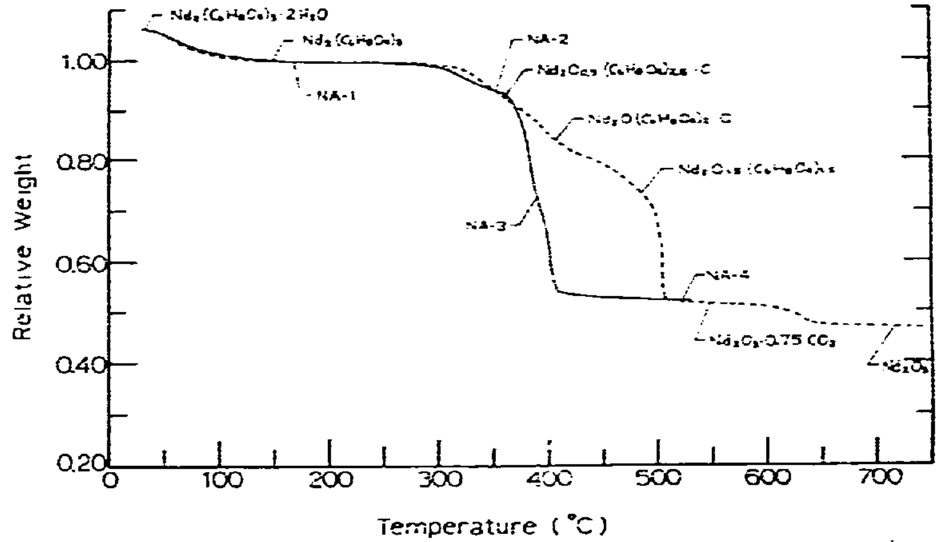


Fig. 4. Thermogravimetric curves for neodymium adipate in air at atmospheric pressure. Curve ———— 4.02 (pH of Pptn.); 25.5 (weight at 180°C, mg); 5 (heating rate, °C min^{-1}). Curve – – – –: 5.36 (pH of Pptn.); 24.8 (weight at 180°C, mg); 5 (heating rate, °C min^{-1}).

Such identification of intermediate forms is further complicated by the presence of a black material, which appeared at temperatures lower than 200°C. Depending on the heating rate, this material persisted to temperatures as high as 500°C. While attempts to isolate the black substance in pure form were unsuccessful, there is little doubt that it was carbon. The presence of carbon in the thermal decomposition of lanthanide oxalates has been reported[3], its suggested source being the disproportionation of CO. Moreover, in this study, infrared absorption spectra of intermediate solid residues in the 200–500°C range show peaks considerably more diffuse than those of starting materials and end products. Especially pronounced for the peaks at 11.4–11.9 μ, this phenomenon could well be due to the scattering of radiation by matter such as carbon. Finally, elemental analyses indicated the presence of free carbon.

All $Pr_2(C_6H_8O_4)_3$ and $Nd_2(C_6H_8O_4)_3$ samples included in this study were stable at temperatures up to 175°C. At 185°C, however, the same samples underwent slow decomposition. Because of this, although somewhat arbitrarily, 180°C has been taken as the temperature at which decomposition starts.

Several residues, reproduced at the heating rate of 5°C min^{-1}, were studied by infrared spectrophotometry and by elemental analysis. Numbers assigned to the samples are indicated in Figs. 2 and 4 at the points of collection.

Infrared curves for $Pr_2(C_6H_8O_4)_3$ are shown in Fig. 5; a similar set for $Nd_2(C_6H_8O_4)_3$ was virtually identical. Special attention was given to absorption bands at wavelengths of about: (a) 3.4 μ, resulting from the carbon–hydrogen stretch and indicative of the presence of organic matter; (b) 6.5 and 7.1 μ, the carbon–oxygen stretch characteristic of lanthanide dicarboxylate compounds; (c) 6.7 and 7.4 μ, the carbon–oxygen stretch characteristic of lanthanide carbonate compounds; and (d) 11.4–11.9 μ, a series of medium intensity peaks exhibited by metal carbonates and said to arise from "internal" vibrations or distortion of the carbonate ion.

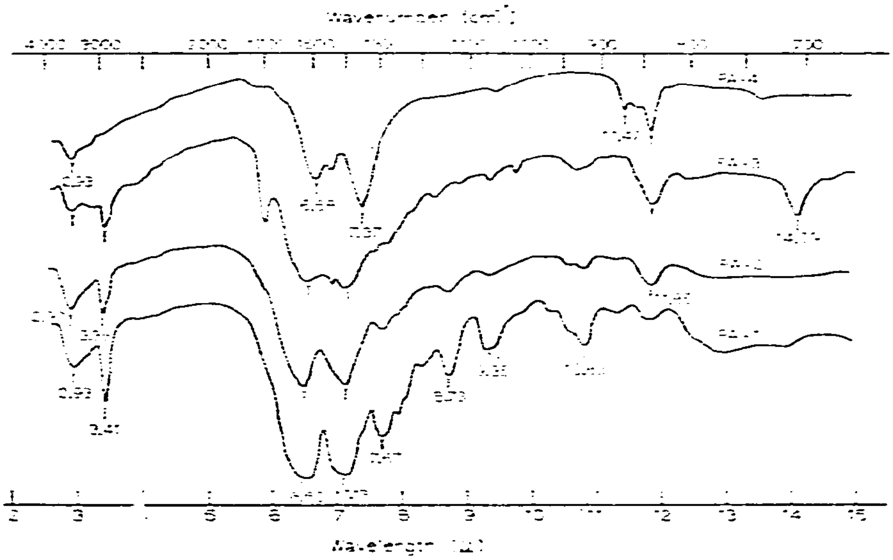


Fig. 5. Infrared absorption spectra for some residual decomposition products of praseodymium adipate precipitated at pH 4.22. PA-1 (205°C); PA-2 (365°C); PA-3 (385°C); PA-4 (440°C).

Apparently, the initial decomposition is to some oxygen-containing intermediate and carbonate begins to form in a step starting at about 360°C. At the same time, the organic nature of the substance persists to temperatures greater than 400°C, at which point the material is completely converted to a carbonate form.

Elemental analyses, completely in keeping with these conclusions, suggested the following representations: PA-1, $Pr_2(C_6H_8O_4)_3$; PA-2, $Pr_2O_{0.5}(C_6H_8O_4)_{2.5}\cdot 1.0C$; PA-4, $Pr_2O_2CO_3\cdot 0.60C$; NA-1, $Nd_2(C_6H_8O_4)_3$; NA-2, $Nd_2O_{0.4}(C_6H_8O_4)_{2.6}\cdot 0.80C$; NA-4, $Nd_2O_2CO_3$.

Elemental analyses were not conclusive for samples PA-3 and NA-3; these samples were obviously non-uniform mixtures and consistent results could not be obtained. A typical set of results (for NA-2) follows:

	Residue (%)	% *Nd*	% *C*	% *H*	% *O*
Calc.	49.5	42.5	29.0	3.1	25.4
Exp.	48.7	42.3	29.0	3.3	25.4

Experimental values for the percent residue were obtained from the thermogravimetric curve; most of those for percent oxygen were obtained by difference. Of interest is the fact that sample NA-2 represented a point where the initial decomposition step was about 80% complete, which is reflected by the empirical formula proposed. Of further interest is the observation that carbon, decreased in amount at 440°C (PA-4), was eliminated at 525°C (NA-4).

Combining the foregoing with relative weights, it is reasonable to postulate at least three steps:

$$Ln_2(C_6H_8O_4)_3 \xrightarrow[36\ min]{180-360°C} Ln_2O_{0.5}(C_6H_8O_4)_{2.5}\cdot C$$

$$Ln_2O_{0.5}(C_6H_8O_4)_3\cdot C \xrightarrow[41\ min]{360-385°C} Ln_2O_{0.5}CO_3(C_6H_8O_4)_{1.5}\cdot C$$

$$Ln_2O_{0.5}CO_3(C_6H_8O_4)_{1.5}\cdot C \xrightarrow[52\ min]{385-440°C} Ln_2O_2CO_3$$

In the decomposition of $Nd_2(C_6H_8O_4)_3$, the absence of a sharp change in slope between 360 and 407°C is not understood. Thermogravimetric curves for other $Nd_2(C_6H_8O_4)_3$ samples, obtained at the same heating rate, show such a change in this temperature range. The form $Ln_2O_2CO_3$ has been observed in the decomposition of many lanthanide compounds, including acetates[17,21], formates[8], other monocarboxylic acid salts[21], carbonates[22–26] and oxalates[4,6,7,10,11].

When heated at the rate of 0.5°C min^{-1}, different intermediates were observed (Figs. 1 and 2). On the basis of relative weights, the following steps are inferred:

$$Ln_2(C_6H_8O_4)_3 \xrightarrow[300\ \mathrm{min}]{180-330\ °\mathrm{C}} Ln_2O_{0.5}(CO_3)_{0.5}(C_6H_8O_4)_2 \cdot C$$

$$Ln_2O_{0.5}(CO_3)_{0.5}(C_6H_8O_4)_2 \cdot C \xrightarrow[380\ \mathrm{min}]{330-370\ °\mathrm{C}} Ln_2O_{0.5}(CO_3)_{2.5}$$

Thermogravimetric curves for $Ln_2(C_6H_8O_4)_3$ samples precipitated at $pH>5$ (Figs. 1–4) are quite different in shape. Relative weights suggest the following transformations at the heating rate of 5 °C min^{-1}:

$$Ln_2(C_6H_8O_4)_3 \xrightarrow[\substack{58\ \mathrm{min\ (Pr)}\\ 61\ \mathrm{min\ (Nd)}}]{180-\left\{\substack{470\ °\mathrm{C\ (Pr)}\\ 485\ °\mathrm{C\ (Nd)}}\right.} Ln_2O_{1.5}(C_6H_8O_4)_{1.5}$$

$$Ln_2O_{1.5}(C_6H_8O_4)_{1.5} \xrightarrow[\substack{59\ \mathrm{min\ (Pr)}\\ 64\ \mathrm{min\ (Nd)}}]{\substack{470-480\ °\mathrm{C\ (Pr)}\\ 485-505\ °\mathrm{C\ (Nd)}}} Ln_2O_2CO_3$$

and at the heating rate of 0.5 C min^{-1}:

$$Ln_2(C_6H_8O_4)_3 \xrightarrow[\substack{320\ \mathrm{min\ (Pr)}\\ 400\ \mathrm{min\ (Nd)}}]{\substack{180-340\ °\mathrm{C\ (Pr)}\\ 180-380\ °\mathrm{C\ (Nd)}}} Ln_2O(C_6H_8O_4)_2$$

$$Ln_2O(C_6H_8O_4)_2 \xrightarrow[330\mathrm{min}]{340-350\ °\mathrm{C\ (Pr)}} Ln_2O_2(C_6H_8O_4)$$

Clearly, the nature of intermediates which show up (however transitory their existence) and, hence, the shape of thermogravimetric curves depends on the pH of precipitation. In general, samples precipitated at lower pH decomposed more readily, i.e. at lower temperatures. As noted earlier, the pH of precipitation was controlled by varying the time during which the hydrolysis of urea was continued after the appearance of precipitate. The attainment of pH values greater than 5.5, for example, required 1–2 hours of additional heating. One might be inclined to attribute the enhanced stability of those precipitates formed at higher pH to the effect of digestion. However, for samples precipitated at pH greater than 5, the evidence suggests no carbonate-containing intermediate before $Ln_2O_2CO_3$, whereas, for samples precipitated at pH less than 5, carbonate-containing intermediates are formed very early in the decomposition. In this respect, the former samples behave much like the corresponding sebacates (Figs. 6 and 7). In consequence, the possibility of fundamental structural differences and a different decomposition mechanism must not be ignored.

In addition, the nature of intermediates and thermogravimetric curve shape varies with heating rate, even for samples precipitated at the same pH. While this

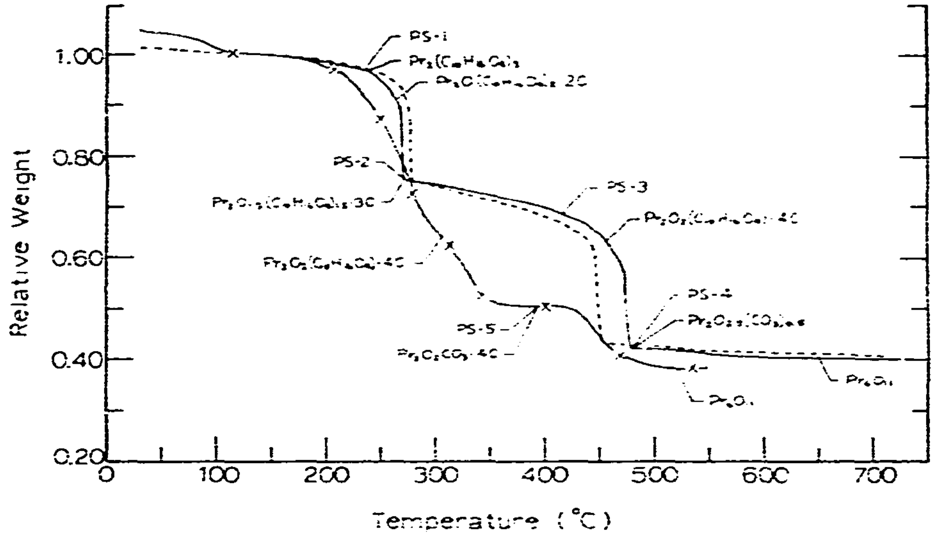


Fig. 6. Thermogravimetric curves for praseodymium sebacate in air at atmospheric pressure. Curve — — — —: 3.61 (pH of Pptn.); 26.1 (weight at 150 °C, mg); 5 (heating rate, °C min^{-1}). Curve ————: 5.47 (pH of Pptn.); 25.2 (weight at 150 °C, mg); 5 (heating rate, °C min^{-1}). Curve — × — ×: 5.47 (pH of Pptn.); 25.2 (weight at 150°C, mg); 0.5 (heating rate, °C min^{-1}).

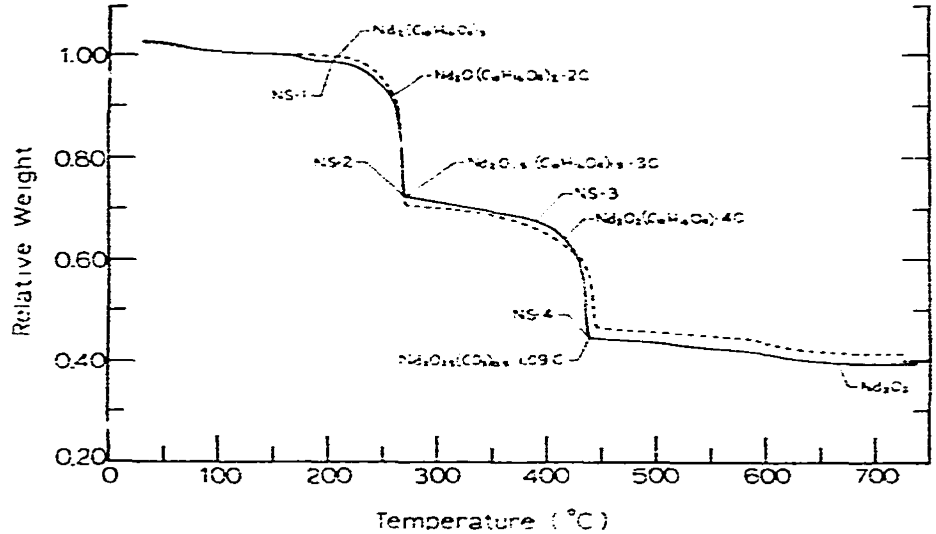


Fig. 7. Thermogravimetric curves for neodymium sebacate in air at atmospheric pressure. Curve ————: 3.80 (pH of Pptn.); 22.7 (weight at 150 °C, mg); 5 (heating rate, °C min^{-1}). Curve — — — —: 5.37 (pH of Pptn.); 24.6 (weight at 150 °C, mg); 5 (heating rate, °C min^{-1}).

phenomenon could reflect an essentially different mechanism (e.g. rate of heat transfer to the interface as opposed to the rate of interface movement, associated respectively with slow and rapid heating rates), it is more likely a function of time and the fact that these are very slow decompositions.

Consider $Pr_2(C_6H_8O_4)_3$ and $Nd_2(C_6H_8O_4)_3$ precipitated at pH greater than 5. Several such samples decomposed isothermally at 185 °C attained relative weights of about 0.78 after one year. At this point, observations were discontinued since the rate of weight loss had become extremely small. At 230 °C, $Nd_2(C_6H_8O_4)_3$ decomposed to a product of relative weight 0.731 after 38 days. The relative weight of $Pr_2O_{1.5}(C_6H_8O_4)_{1.5}$ is 0.731; that of $Nd_2(C_6H_8O_4)_3$ is 0.733. It is very likely then, that $Ln_2O_{1.5}(C_6H_8O_4)_{1.5}$ is a product of both decompositions. The same form showed up at about 470 °C when $Pr_2(C_6H_8O_4)_3$ was decomposed at heating rates of 5 °C min^{-1} and 10 °C min^{-1} (Fig. 2), corresponding to 58 min and 29 min, respectively. At temperatures greater than 470 °C, it decomposed rapidly to $Ln_2O_2CO_3$. If $Ln_2O_{1.5}(C_6H_8O_4)_{1.5}$ is formed in decompositions conducted both isothermally and at high heating rates, it was almost certainly present in the decomposition of the same $Pr_2(C_6H_8O_4)_3$ sample at 0.5 °C min^{-1} (Fig. 1) at about 350 °C. The absence of any abrupt change in slope in the curve at that point indicates that $Ln_2O_{1.5}(C_6H_8O_4)_{1.5}$ is unstable at that temperature and that, unlike in the temperature range 400–470 °C, its formation is so slow that the transformation $Ln_2O_{1.5}(C_6H_8O_4)_{1.5} \rightarrow Ln_2O_2(C_6H_8O_4)$ occurs simultaneously.

The same argument can be applied throughout all these decompositions Two conclusions result. First, only the duration of existence and not the nature of intermediates depends on the heating rate. Hence, the decomposition mechanism is unchanged by variations in the heating rate. Secondly, the detection of intermediates is ameliorated by observations at at least two rather widely separated heating rates.

Reasonable mechanisms, comprising information obtained at all heating rates, may be proposed. Carbon is not included since the degree to which it is formed varies with temperature which, in turn, depends on heating rate. For samples precipitated at pH<5:

$$\begin{tikzcd}
Ln_2(C_6H_8O_4)_3 \arrow[r] & Ln_2O_{0.5}(C_6H_8O_4)_{2.5} \arrow[r] & Ln_2O_{0.5}(CO_3)_{0.5}(C_6H_8O_4)_2 \arrow[d] \\
Ln_2O_2CO_3 \arrow[dr] \arrow[ddr] & Ln_2O_{0.5}(CO_3)_{2.5} \arrow[l] & Ln_2O_{0.5}(CO_3)(C_6H_8O_4)_{1.5} \arrow[l] \\
 & Pr_6O_{11} & \\
 & Nd_2O_3 &
\end{tikzcd}$$

For samples precipitated at pH>5:

$$\begin{tikzcd}
Ln_2(C_6H_8O_4)_3 \arrow[r] & Ln_2O(C_6H_8O_4)_2 \arrow[r] & Ln_2O_{1.5}(C_6H_8O_4)_{1.5} \arrow[dd] \\
Pr_5O_{11} & & \\
 & Ln_2O_2CO_3 \arrow[ul] \arrow[dl] & Ln_2O_2(C_6H_8O_4) \arrow[l] \\
Nd_2O_3 & &
\end{tikzcd}$$

$Pr_2(C_{10}H_{16}O_4)_3$ and $Nd_2(C_{10}H_{16}O_4)_3$ samples studied differed from the corresponding adipates in at least three ways. First, isothermal studies indicated that decomposition starts at temperatures much lower than 175 °C. In fact, there may be no temperature greater than 100 °C at which these compounds are thermally stable. Moreover, the thermal decomposition pattern, curves for which are shown in Figs. 6 and 7, is independent of pH of precipitation. Finally, and most confounding of all, it appears that normal sebacates were not formed. Such a conclusion results from consistently high relative weights of the products of ignition as well as from elemental analyses.

Possibly the preparation of only basic sebacates was due to the washing process. When the solutions from which the precipitates were formed were cooled, the precipitates became contaminated with rather large amounts of unreacted sebacic acid, virtually none of which could be removed by washing with acetone. In addition, washing with ethanol and ether was not completely effective in this application. As a result, the precipitates were washed with hot water and, because of the low solubility of sebacic acid, with copious quantities at that.

The use of basic sebacates in thermal decomposition studies can provide worthwhile information. If, for the compounds represented in Figs. 6 and 7, a constant mole fraction of Ln_2O_3, consistent with relative weights and elemental analyses, is assumed, it is possible to deduce a decomposition pattern.

The results of elemental analyses suggest the following forms:

Sample	*Temp (°C)*	*Form*
PS-0	25	$0.943\ Pr_2(C_{10}H_{16}O_4)_3 \cdot 0.0571\ Pr_2O_3$
NS-0	25	$0.926\ Nd_2(C_{10}H_{16}O_4)_3 \cdot 0.0741\ Nd_2O_3$
PS-1	235	$0.943\ Pr_2(C_{10}H_{16}O_4)_3 \cdot 0.0571\ Pr_2O_3$
NS-1	205	$0.926\ Nd_2(C_{10}H_{16}O_4)_3 \cdot 0.0741\ Nd_2O_3$
PS-2	270	$0.943\ Pr_2O_{1.5}(C_{10}H_{16}O_4)_{1.5} \cdot 0.0571\ Pr_2O_3 \cdot 3C$
NS-2	270	$0.926\ Nd_2O_{1.5}(C_{10}H_{16}O_4)_{1.5} \cdot 0.0741\ Nd_2O_3 \cdot 3C$
PS-4	480	$0.943\ Pr_2O_{2.5}(CO_3)_{0.5} \cdot 0.0571\ Pr_2O_3 \cdot 0.349C$
NS-4	440	$0.926\ Nd_2O_{2.5}(CO_3)_{0.5} \cdot 0.0741\ Nd_2O_3 \cdot 1.09C$

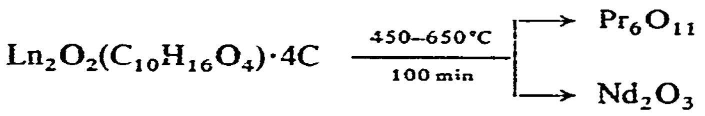
Note that carbon formed at temperatures below 270 °C is partially gone at 440 °C and more extensively removed at 480 °C. Note further that these forms are consistent with infrared absorption spectra, shown for $Nd_2(C_{10}H_{16}O_4)_3$ in Fig. 8; those for $Pr_2C_{10}H_{16}O_4)_3$ are nearly identical. Carbonate does not show up at temperatures below 400 °C.

On the basis of the foregoing and as a result of the formation of products corresponding to $0.943\ Pr_2O_2(C_{10}H_{16}O_4) \cdot 0.0571\ Pr_2O_3$ and to $0.926\ Nd_2O_2(C_{10}H_{16}O_4) \cdot 0.0741\ Nd_2O_3$, the following decomposition path is proposed:

$$Ln_2(C_{10}H_{16}O_4)_3 \xrightarrow[20\ \text{min}]{150\text{–}250\,^\circ\text{C}} Ln_2O(C_{10}H_{16}O_4)_2 \cdot 2C$$

$$Ln_2O(C_{10}H_{16}O_4)_2\cdot 2C \xrightarrow[20\ min]{250\,^{\circ}C} Ln_2O_{1.5}(C_{10}H_{16}O_4)_{1.5}\cdot 3C$$

$$Ln_2O_{1.5}(C_{10}H_{16}O_4)_{1.5}\cdot 3C \xrightarrow[60\ min]{250\text{–}450\,^{\circ}C} Ln_2O_2(C_{10}H_{16}O_4)\cdot 4C$$



$$Ln_2O_2(C_{10}H_{16}O_4)\cdot 4C \xrightarrow[100\ min]{450\text{–}650\,^{\circ}C} \begin{cases} Pr_6O_{11} \\ Nd_2O_3 \end{cases}$$

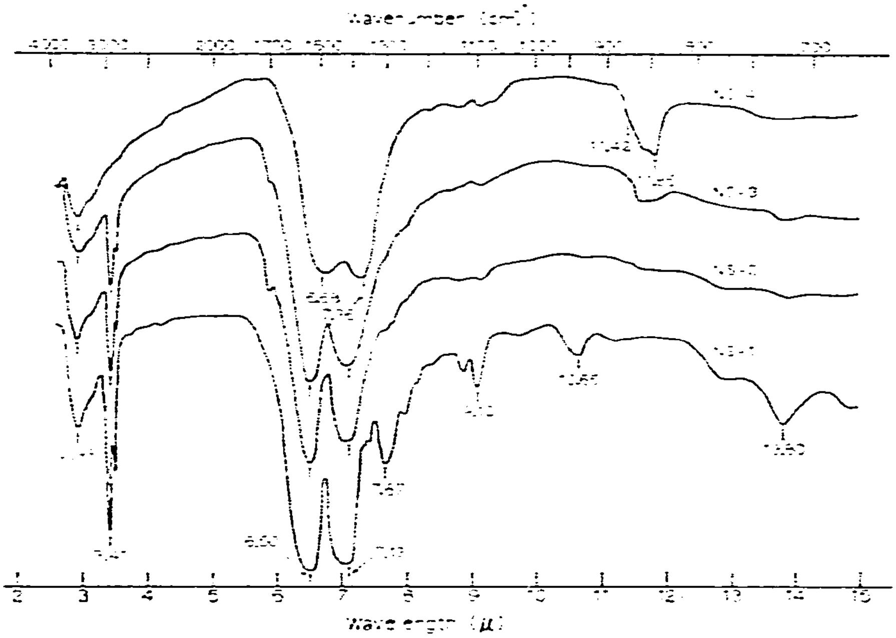


Fig. 8. Infrared absorption spectra for some residual decomposition products of neodymium sebacate precipitated at pH 3.80. NS-1 (205 °C); NS-2 (270 °C); NS-3 (390 °C); NS-4 (440 °C).

The intermediate $Ln_2O_2CO_3$, which showed up at the heating rate of 0.5 °C min^{-1} did not appear at the higher heating rate. Clearly, in the latter case, it could not have formed until temperatures greater than 450 °C had been attained and at this temperature it is not stable.

It would appear that, although both show the same intermediates, $Ln_2(C_6H_8O_4)_3$ precipitated at $pH > 5$ is more stable than $Ln_2(C_{10}H_{16}O_4)_3$ in that the latter decomposes at somewhat lower temperatures. The fact that the same intermediates appear, however, indicates a similarity in structure.

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